

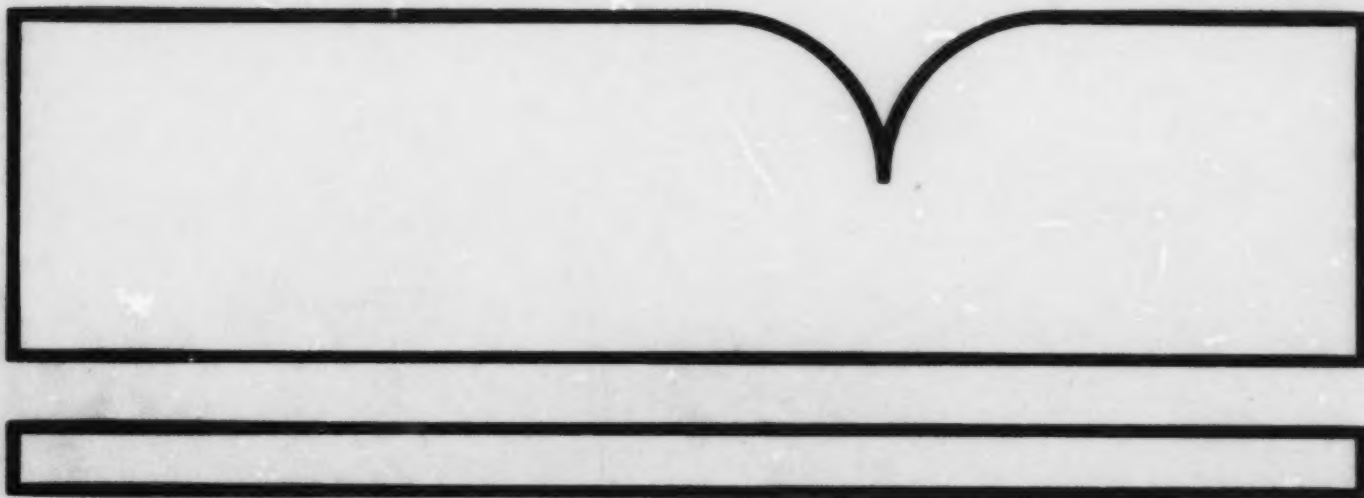
The IJC Menomonee River Watershed Study
Atmospheric Chemistry of Lead and Phosphorus
Volume 8

Wisconsin Univ.-Madison

Prepared for

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Agency

Great Lakes National
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Volume 8



The IJC Menomonee River Watershed Study



Atmospheric Chemistry Of Lead And Phosphorus



Menomonee River ★

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques, and new technologies through which optimum use of the nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

The Great Lakes National Program Office (GLNPO) of the U.S. EPA, was established in Region V, Chicago to provide a specific focus on the water quality concerns of the Great Lakes. GLNPO also provides funding and personnel support to the International Joint Commission activities under the U.S.- Canada Great Lakes Water Quality Agreement.

Several land use water quality studies have been funded to support the pollution from Land Use Activities Reference Group (PLUARG) under the Agreement to address specific objectives related to land use pollution to the Great Lakes. This report describes some of the work supported by this Office to carry out PLUARG study objectives.

We hope that the information and data contained herein will help planners and managers of pollution control agencies make better decisions for carrying forward their pollution control responsibilities.

Madonna F. McGrath
Director
Great Lakes National Program Office

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Volume 8

by

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Water Resources Center and
Water Chemistry Program

for

U.S. Environmental Protection Agency
Chicago, Illinois

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Grants Officer
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Great Lakes National Program Office

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This report has been reviewed by the Great Lakes National Program Office of the U.S. Environmental Protection Agency, Region V Chicago, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

PREFACE

The importance of air pollution to the direct and indirect loadings of lead and phosphorus to Lake Michigan is evaluated utilizing dry and wet deposition information obtained in the Menomonee River Watershed.

CONTENTS

Title Page	1
Disclaimer	11
Preface	111
Contents	iv
Acknowledgement	v
*Part I - Atmospheric Monitoring Program	I-1
*Part II - Lead Deposition to the Watershed	II-1
*Part III - Lead Deposition to Lake Michigan	III-1
*Part IV - Total Phosphorus Loadings to the Watershed	IV-1
*Part V - Atmospheric Chemistry of Lead and Phosphorus.	V-1

*Detailed contents are presented at the beginning of each part.

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PART I
ATMOSPHERIC MONITORING PROGRAM

by

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ABSTRACT

Air monitoring stations were located in five different land use types of the Menomonee River Watershed. Total suspended particulate concentrations were highest in the industrial valley, decreasing to the residential, transition-urban, mixed rural and rural. Even the rural station experienced effects from local urban emission sources. All stations exhibited similar temporal trends of suspended load.

The concentration of lead in rain was consistently at about 30 $\mu\text{g/L}$. There were no obvious differences corresponding to land use type.

A method for accurately establishing the weight of air particulate matter collected on filters has been developed by constructing a clean glove box. The system is capable of maintaining a constant relative humidity and temperature. A description of this system is presented.

CONTENTS - PART I

Title Page	I-i
Abstract	I-ii
Contents	I-iii
Figures	I-iv
Tables	I-v
I-1. Introduction	I-1
I-2. Conclusions	I-3
I-3. Methods and Procedures	I-4
Total Suspended Particulates	I-4
Rain	I-4
Equipment	I-4
Field procedures	I-5
Analysis	I-5
Clean laboratory procedure	I-5
I-4. Results and Discussion	I-7
Total Suspended Particulates	I-7
Rain	I-7
References	I-13
Appendix	
I-A. A Constant Relative Humidity-Temperature Chamber for the Accurate Weight Determination of Air Particulate Matter Collected on Filters	I-14

FIGURES

<u>Number</u>		<u>Page</u>
I-1	Location of air and rain monitoring stations	I-2
I-2	Total suspended particulate concentrations for sites at 70th Street, Appleton Avenue and Donges Bay Road	I-9
I-3	Total suspended particulate concentrations for sites at Falk Corporation and River Lane	I-10
I-4	Concentration of lead in rain as related to the amount of rain	I-12
I-A-1	Diagram of the constant relative humidity-temperature chamber	I-15

TABLES

<u>Number</u>		<u>Page</u>
I-1	Arithmetic means for 21 sampling periods for total suspended particulate concentrations	I-8
I-2	Arithmetic mean concentrations of several constituents in rain	I-11

I-1. INTRODUCTION

The Menomonee River Watershed is characterized by five major land use types: heavy industrial, residential, transition-urban, mixed rural, and rural. Samplers designed to collect rain and atmospheric particulate matter were located in each of these areas for the purpose of investigating local effects on air pollutant levels. Figure I-1 indicates the air monitoring stations in the watershed. The sampling locations, corresponding to land use types, are: Falk Corporation, 70th St., Appleton Ave., River Lane and Donges Bay Road, respectively. The duration of the investigation was from 9/76-9/77.

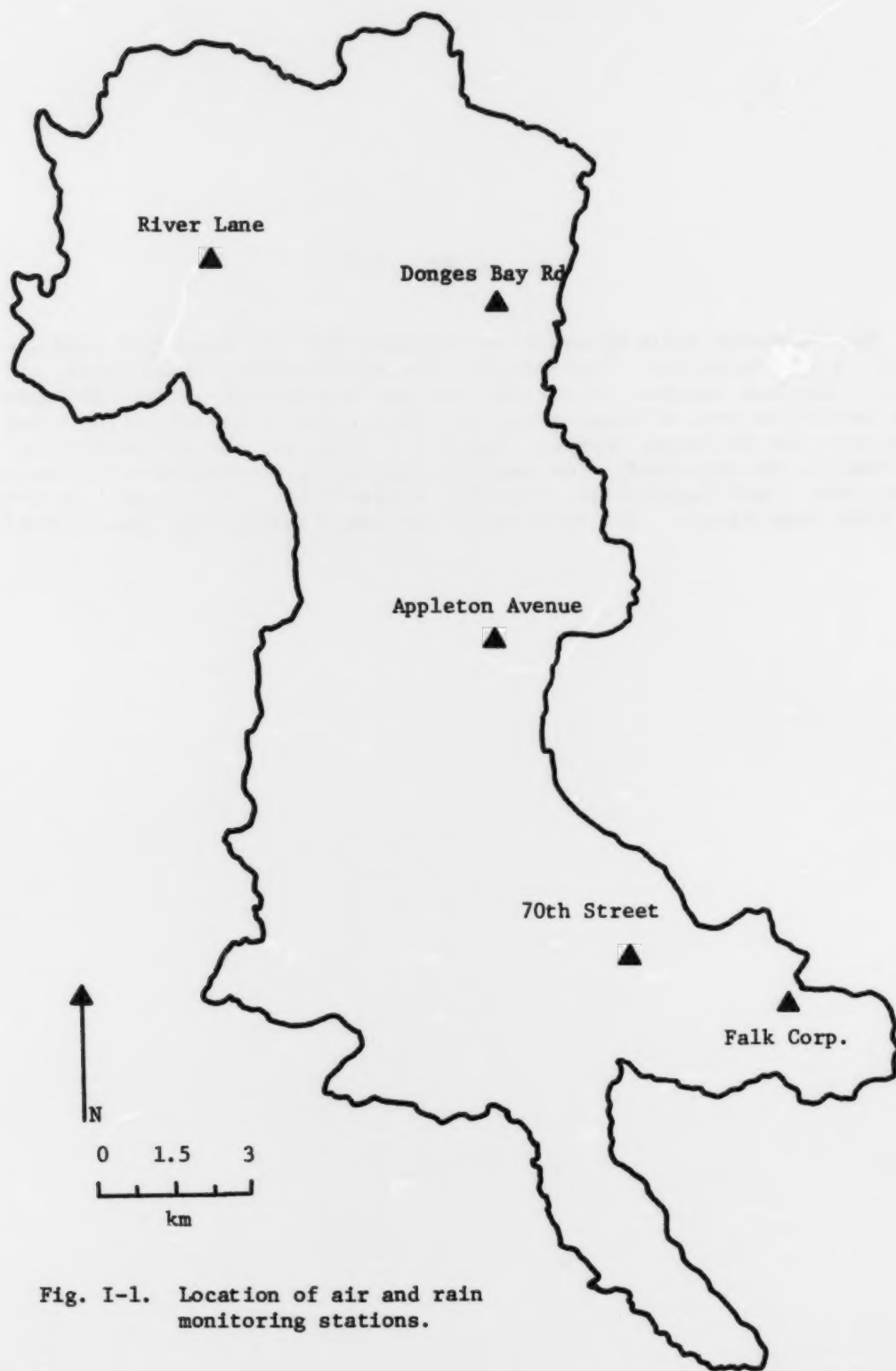


Fig. I-1. Location of air and rain monitoring stations.

I-2. CONCLUSIONS

Average total suspended particulate (TSP) concentrations found in air for the period 9/76-9/77 at each station is a function of land use types. The highest average concentrations were measured at the heavy industrial site, with a progressive decrease from residential, transition-urban, mixed-rural, to rural sites. The total suspended load in air decreases by an average of 50% from the heavy industrial site at the Falk Corporation to the rural station at Donges Bay Road, a distance of approximately 24 km. Nevertheless, it is apparent that concentrations measured at Donges Bay Road are influenced by the proximity of local urban emission sources during certain wind conditions and the average background level of suspended particulate matter for this area is in the range of 35 to 40 $\mu\text{g}/\text{m}^3$.

The observed region-wide trends for TSP are thought to be the result of two phenomena: a. Meteorological conditions affect the dispersion of locally-emitted pollutants. The concentration of suspended particulate matter is increased by low wind speeds and mixing height even though local emission rates remain constant: b. Of secondary importance are the influences of large air masses with characteristically higher pollutant loads compared to average background levels. It is expected that air masses originating from large urban centers such as Chicago or St. Louis carry higher pollutant loads into the Watershed than winds from the northwest.

The spatial and temporal concentrations of lead in rain did not exhibit marked trends or variations. The measured level was consistently around 30 $\mu\text{g}/\text{L}$ with a range of 10 to 130 $\mu\text{g}/\text{L}$. The measured concentration of any trace constituent in rain seems to be a function of many parameters and it is difficult to quantify the effect of land use type or meteorological factors.

I-3. METHODS AND PROCEDURES

Total Suspended Particulates

Total suspended particulate (TSP) samples were collected with high volume air samplers. Operationally, 30 ft³/min (1 m³/min) of air is drawn through a 9 x 7 inch (23 x 18 cm) surface of Whatman 41 cellulose filter for approximately 48 hr during the summer and 72 hr during the winter. The flow is maintained at a constant rate with a mass flow controller.

Filters are transported and stored in plastic zip-lock bags; handling is carried out with plastic gloves or plastic coated tweezers. Hygroscopicity can be a major problem in gravimetric analysis. In Appendix I-A proper handling methods are discussed which overcame ambient humidity fluctuations.

Rain Sampling

Equipment

The Wang rain sampler was chosen after careful consideration of monitoring and analysis needs. The desired system must meet three criteria, namely, a. be non-contaminating for lead, b. collects only rain and excludes fugitive dust and c. minimizes evaporative losses.

The Wang sampler, features an aluminum sliding cover triggered to open by a moisture-sensing head. A heating coil within the head drives off residual moisture following an event, which allows the cover to close during dry periods.

The original collection apparatus was modified to meet the guidelines stated above. Rain was collected in a linear polyethylene (LPE) funnel. A small glass funnel is heat-embedded in the neck of the plastic funnel. Attached to the neck of the glass funnel is 1/8" (0.32 cm) i.d. Tygon tubing leading to a 2-L LPE collection bottle. A vent, of the same diameter as the tube, protrudes from the cap, allowing air to escape while filling, and acting as an overflow valve for large events.

A gap existed between the sliding cover and the sampler body in the original equipment. With this configuration, wind-blown fugitive dust conceivably could contaminate the rain samples. To prevent the problem, foam covered by plastic was taped to the body, forming a virtual seal with the

closed lid. This minimized evaporation losses, as did the small bore tubing which limited the exposed surface area.

It was anticipated that the samplers would operate reliably since an earlier investigation by Galloway and Likens (1) had ranked the Wang sampler first among the wet-only samplers tested for functional reliability. In fact, there were few electronic problems and the mechanical difficulties encountered resulted from the modifications.

Field procedures

Sample collection flasks were changed weekly unless insufficient volume (< 75 ml) was collected. Samples are therefore composites of all events that occurred during the period. It is evident that collection flasks from each station must be changed at the same time in order to make loading comparisons.

Freezing conditions precluded operations from 12/1/76 to 4/12/77. Even during the warmer months, a frozen lid due to extreme heat is probably the single greatest factor contributing to sampling error. Several very large events occurred in 1977 which caused the collection flasks to overflow but this was the exception rather than the rule.

Some loss of quality control occurred in late 1977 when other investigators removed aliquots from the collection flasks on an erratic basis for other analyses. Additionally, some rain was stored in plastic bottles with cardboard liners in the caps. These bottles may have adsorbed Pb^{++} or contaminated samples to an unknown extent.

The rain samples were usually acidified directly in the collection flask to a pH of 1 with HNO_3 , transferred to other LPE containers and weighed to ascertain volume. Samples were stored at $4^{\circ}C$ prior to analysis.

Analysis

Lead was measured by injecting rain directly into a graphite furnace atomizer of an atomic absorption spectrometer. Background absorption was negligible for all samples and wavelengths checked. Standard additions of lead yield very similar values to measurements obtained using a standard curve. Both results verify that the total ion matrix in rain is dilute.

Clean laboratory procedure

All sample containers were made of linear polyethylene and were cleaned by soaking for at least 24 hr in 10% HNO_3 before use. After soaking, water distilled three times was used to rinse them. Finally the containers were air-dried upside down.

All water used for standards and rinsing was triple distilled. Primary

distilled water was passed through a glass still. This distillate was further purified in a sub-boiling quartz still. The hazard of contamination is most severe for cadmium and sodium at the levels found in rainwater.

I-4. RESULTS AND DISCUSSION

Total Suspended Particulates

Table I-1 lists the arithmetic mean values of the total suspended particulate concentrations from 21 sampling periods. Ranked by land use type from high to low, the heavy industrial site at Falk Corporation consistently is highest followed by residential, transition-urban, mixed rural and rural. The frequency of sampling periods for which this order was exactly followed was 43% of the time.

All stations exhibit a similar trend in the suspended load from one sampling interval to the next. Figure I-2 shows the results from three stations. The same trends are observed even for the two most distant stations (Fig. I-3). Evidently regional conditions are primarily responsible for the episodes of increased pollutant levels in air. Figure I-3 also illustrates the consistently higher TSP levels in the industrial valley in contrast to the mixed-rural site.

Rain

Mean concentrations of lead together with several other constituents in rain collected in the Menomonee River Watershed are listed in Table I-2. Lead concentrations exhibit only a few extreme values and consistently approximate 30 $\mu\text{g/L}$.

One might expect that the average concentration of lead in rain would show a marked difference for different land use areas. This concept is very difficult to demonstrate since concentrations observed in rain are a function of many variables, including local sources and rainfall intensity. Consequently, it is difficult to show a relationship between rainfall amount and concentration of pollutants. For one particular sampling interval (9/1 to 9/15/76), lead concentration seemed to be a function of rainfall amount (Fig. I-4) but this was an unusual case.

In general, the concentrations of trace metals, particularly lead, were fairly consistent temporally and spatially. Hence, seasonal trends or variations due to land use type were not obvious during the time period of the investigation. Overall mean concentrations seem to be representative of levels encountered at any place or time in the Watershed.

Table I-1. Arithmetic means of 21 sampling periods for total suspended particulate concentrations

Station	Total suspended particulates, $\mu\text{g}/\text{m}^3$
Falk Corporation	87
70th Street	61
Appleton Avenue	55
River Lane	51
Donges Bay Road	43

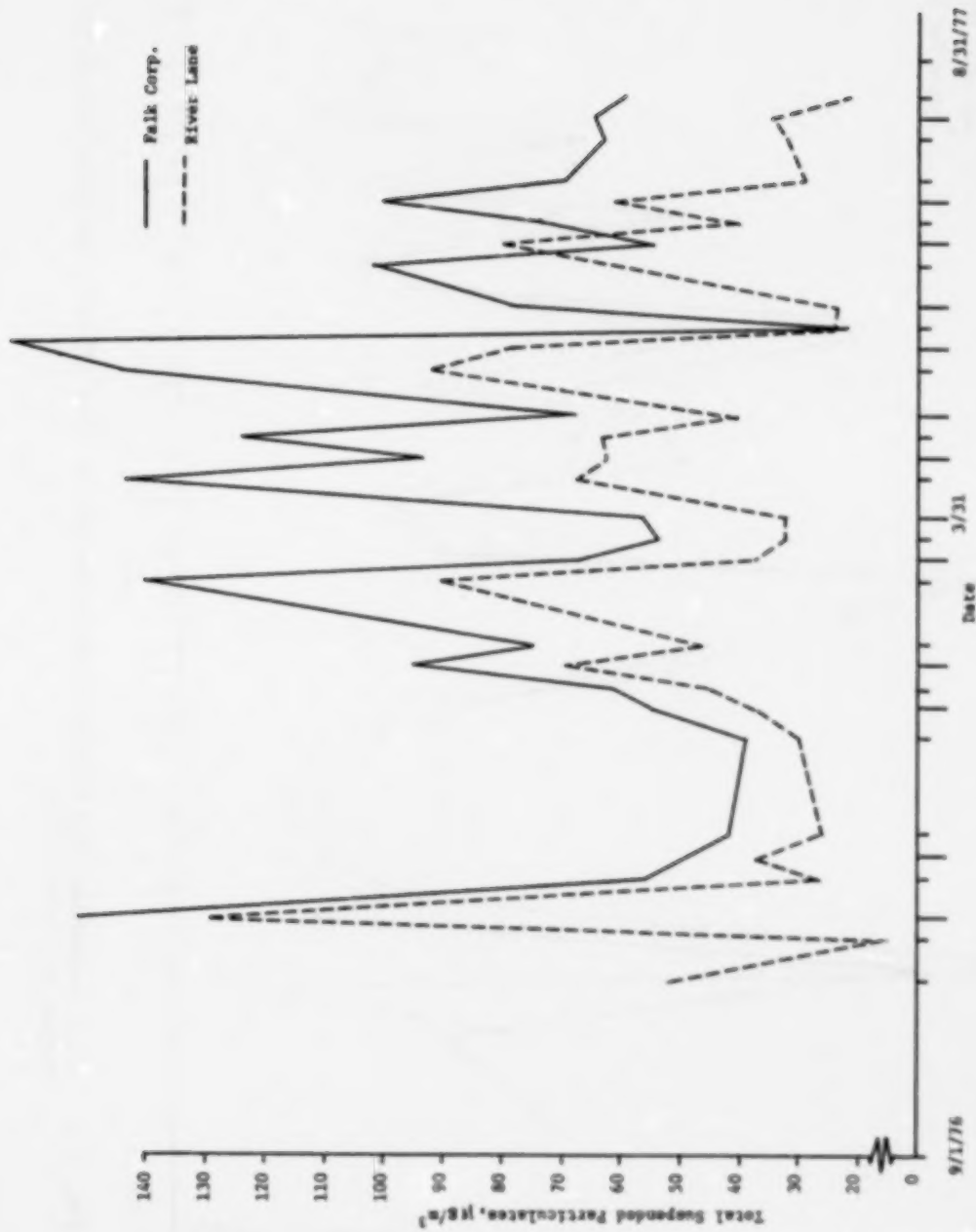


Fig. I-3. Total suspended particulate concentrations at the Falc Corporation and River Lane sites.

Table I-2. Arithmetic mean concentrations
of several constituents in rain

Parameter	Concentration, $\mu\text{g/L}$
Pb	3.2
Cd	3.7
Ca	800
Mg	280
Na	120

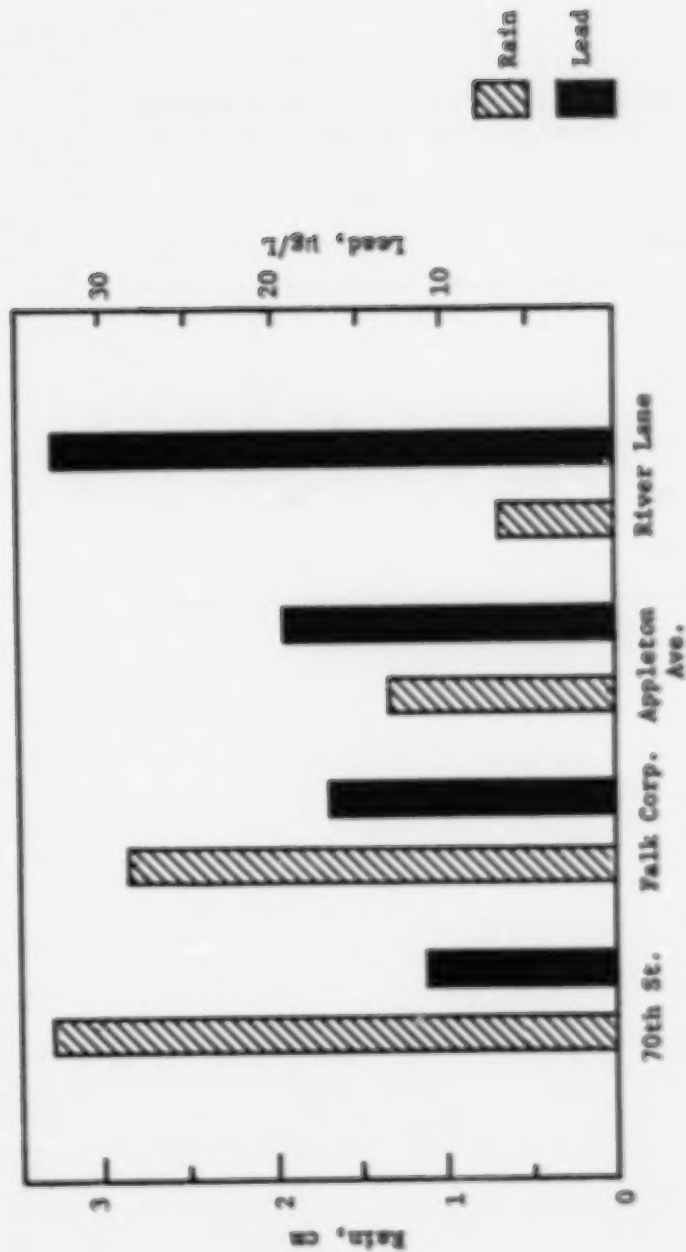


Fig. I-4. Concentration of lead in rain as related to the amount of rain for the sampling interval 9/1 to 9/15/76.

REFERENCES - I

1. Galloway, J. N. and G. E. Likens. Calibration of Collection Procedures for the Determination of Precipitation Chemistry. *Water, Air and Soil Pollution* 6:241-258, 1976.

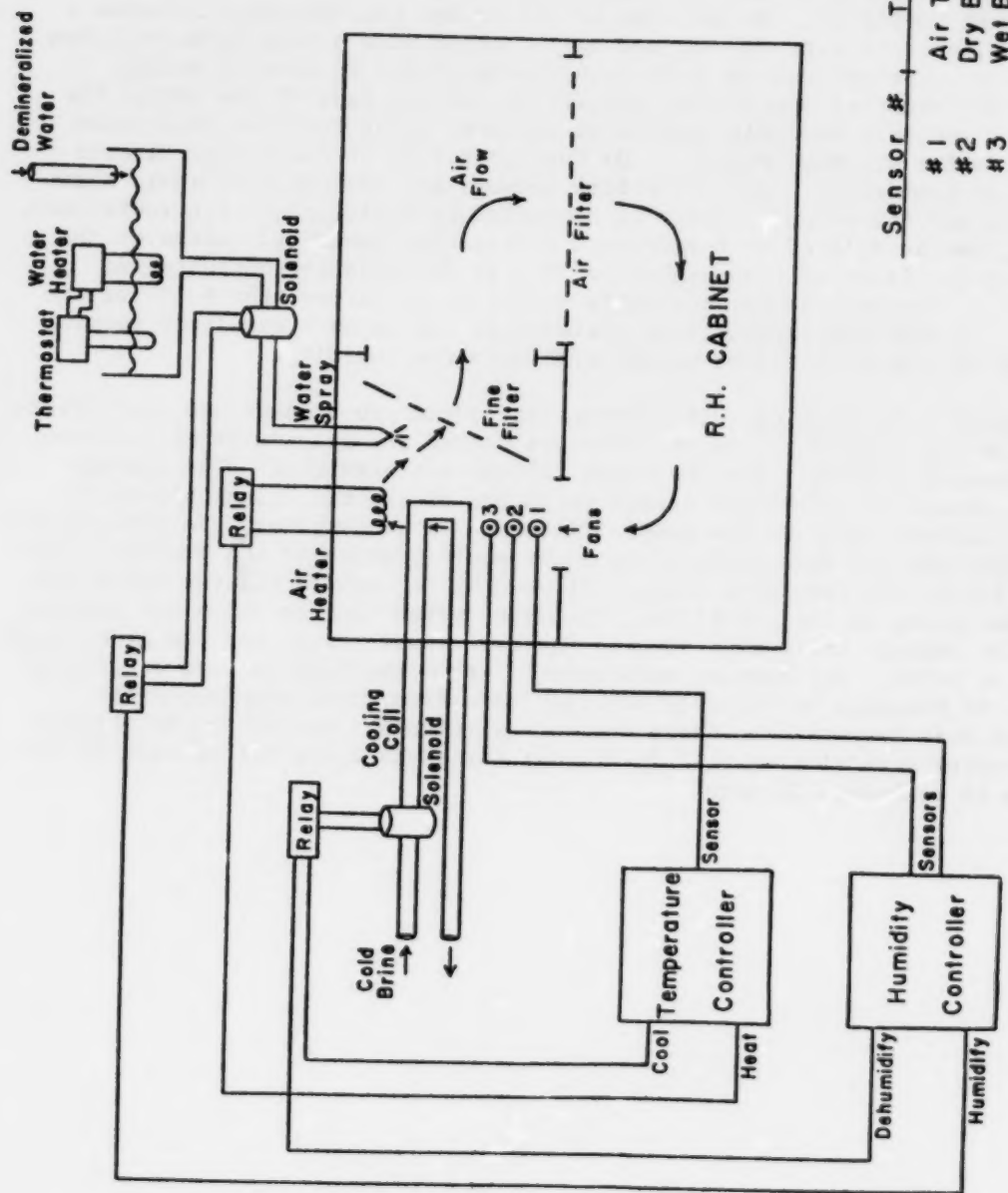
APPENDIX I-A. A CONSTANT RELATIVE HUMIDITY-TEMPERATURE
CHAMBER FOR THE ACCURATE WEIGHT DETERMINATION OF AIR
PARTICULATE MATTER COLLECTED ON FILTERS

Investigators involved with measuring particulate matter in air by high volume samplers must select filters characterized by high collection efficiency, high flow rate, low elemental blank values, and ease of handling. Glass fiber filters are adequate for measurement of many of the above physical criteria and are used widely for total particulate and organic matter although the lower particle cut-off size, with sampling time, is not well known. The high inorganic blank values of glass fiber filters, preclude their use for measuring concentrations of many elements in air. Other filters that have been used include Whatman 41 ashless cellulose, Nucleopore, Millipore, Misco and Delbag microsorban filters. The choice of a particular filter must be guided by the particular sampling program and the analytical objectives. Because of their high pressure drops, Nucleopore and Millipore membrane filters cannot be used when high flow rates are required. Particle bounce-off also occurs with these filters especially when used in cascade impactors^a. It was found that Whatman 41 filters are quite acceptable for high volume air filtration and as substrates for cascade impactors. Their hygroscopic nature can lead to unacceptable weighing errors unless strict precautions are taken^b. Sampling periods of 24 hr usually yield from 20 to 500 mg air particulate matter in the areas sampled while 20 x 25 cm cellulose filters weigh around 4250 mg. Thus, small weighing errors of filters result in large discrepancies. It has been shown that a change of a few percent in relative humidity from tare to gross weighing conditions may introduce weighing errors in collected material ranging from 20 to 200%. It is imperative that constant temperature and humidity conditions be maintained during tare and gross weighing. To overcome this problem a glove box has been constructed which is capable of maintaining a clean environment and constant relative humidity and temperature for weighing operations.

The clean box, 120 x 90 x 90 cm is made from sheet metal, angle iron, and plexiglass plastic. Figure I-A-1 illustrates the essential components of the system. Beginning at the rear of the chamber, conditioned air is circulated through glass fiber filters into the front work space. The analytical balance and work space are accessible through the plexiglass window by two glove ports and a removable door. The chamber air is drawn by fans over heating, cooling

^aDemynek, M. Determination of Irreversible Adsorption of Water by Cellulose Filters. Atmospheric Environment 9:523-528, 1975.

^bDzubay, T. G., L. E. Hines and R. K. Stevens. Particle Bounce Errors in Cascade Impactors. Atmospheric Environment 10:229-234, 1976.



Sensor #	Type
# 1	Air Temperature
# 2	Dry Bulb
# 3	Wet Bulb
	Humidity

Fig. I-A-1. Diagram of the constant relative humidity-temperature chamber.

and humidifier sensors. These sensors consist of two sets of precision thermistors (YSI 44004). One set (three in each set) is dedicated to sensing temperature and humidity and the other serves as the chamber operating sensors through feedback loops. The individual thermistors thus function as air temperature, dry bulb and wet bulb indicators.

The temperature sensor is linked to a bridge circuit differential operational amplifier. On one side of the bridge the amplifier actuates a heating element to warm the air and on the other side a cold brine solution to cool it. The wet and dry bulb sensors are linked to another bridge circuit differential operational amplifier. On one side of the bridge the amplifier controls dehumidification of the air, using the same cold brine that cools the air temperature. On the other side of the bridge circuit the air is humidified. The analytical sensors are connected to strip chart recorders and the output voltage is converted to resistance. The resistance, in turn, can be related to temperature or relative humidity. Although the long term precision of the chamber is $50 \pm 3\%$ for relative humidity and $25 \pm 0.5^\circ\text{C}$ for temperature, the daily variation is better than $\pm 1\%$ for the former. In addition, appropriate corrections can be made easily by knowing the rate of change of filter weight with relative humidity.

Before tare weighing, all filters, including two blanks, are equilibrated inside the chamber for 24 hr. The two blanks are weighed first followed by the sample filters. The two blank filters are reweighed. The average change between the first and second weighings of the two filter blanks is applied incrementally to the sample filters. After sampling, the gross weight determinations are made again after 24 hr equilibration in the chamber. The blank filters are reweighed first, followed by the sample filters and a further reweighing of the two blanks; the same corrections as above are applied. Also, the average difference between the tare blank weight and the gross blank weight is noted. All samples subsequently are normalized to tare conditions when it is possible to directly subtract tare from gross sample weights. Repeated measurements have shown that air particulate matter can be weighed with greater precision than 1% (± 0.1 mg) for glass fiber filters and 7% for Whatman 41 cellulose filters.

PART II
LEAD DEPOSITION TO THE WATERSHED

by

T. R. STOLZENBURG
A. W. ANDREN

ABSTRACT

The wet deposition of lead to the Watershed is calculated directly from measurements in rain. Dry deposition from long range sources is distinguished from lead originating within the Watershed. Most atmospherically-derived lead deposited in the Watershed does not reach Lake Michigan.

CONTENTS - PART II

Title Page	II-1
Abstract	II-11
Contents	II-111
II-1. Introduction	II-1
II-2. Conclusions	II-2
II-3. Calculation and Discussion	II-3
Deposition	II-3
Delivery	II-4
References	II-5

II-1. INTRODUCTION

Suspended dust concentrations in themselves are important for human health reasons. However, deposition calculations must be made in order to assess the impact of airborne pollutants on water quality. Atmospheric lead is removed from the atmosphere to the Watershed through wet and dry processes. Both modes of transport to the surface must be accounted for when calculating total flux.

Deposition by wet processes can be measured directly using wet only samplers. Deposition by dry processes is difficult to measure directly owing to the wide variety of natural impaction surfaces in the environment, i.e., water, grass, concrete, etc. Several investigators have made reasonable estimates of lead flux to the surface (1,2) for Lake Michigan and rural Illinois, respectively. In both studies, it is evident that most of the lead originated from distant sources even though automotive exhaust represents a large source of lead deposited in the watershed.

II-2. CONCLUSIONS

Atmospheric lead is deposited on the Menomonee River Watershed by wet and dry processes from distant sources at the rate of 1.4×10^6 kg/yr or 400 g/ha-yr. Of this amount, less than half reaches Lake Michigan.

Automotive exhaust from vehicular traffic in the Watershed contributes an additional 7.9×10^6 kg/yr of lead to the Watershed. The delivery ratio of lead to the river is probably quite high because the natural removal processes (filtration, coagulation, adsorption and biological uptake) are bypassed.

II-3. CALCULATION AND DISCUSSION

Deposition

Of the metals and nutrients studied only lead and phosphorus have significant atmospheric inputs relative to weathering and point sources at the land surface. Phosphorus deposition is dealt with later.

The rain sampling program undertaken permits measurement of lead concentrations and hence direct calculation of input of lead by precipitation. Based on a mean concentration of 30 $\mu\text{g/L}$ and an annual precipitation total of 76.2 cm, lead loading to the Watershed by precipitation is 230 g/ha-yr.

Dry deposition is a function of the suspended concentration and the deposition velocity of particles containing lead. Based on current investigations and those of Hudson et al (2) and Andren et al (1), the dry deposition rate for lead is approximately 180 g/ha-yr. Overall, lead enters the Watershed through the atmosphere at a rate of approximately 400 g/ha-yr or 1.4×10^4 kg/yr.

However, the dry deposition estimates represent only lead from long range transport (i.e. based on deposition calculations for Lake Michigan). Much of the measured lead in precipitation falls into this same category. Hence the lead input figure of 1.4×10^4 kg/yr (400 g/ha-yr) includes only that lead originating from outside the Watershed.

Clearly there exists a large near-ground source of lead from vehicular traffic in the Watershed. The investigations of Habibi (3,4) demonstrate that most of the lead from automobile exhausts is deposited within a few meters of the highway. Therefore, the additional pertinent calculations are the amount of lead emitted and remaining within the Watershed. The methodology described by Huntzicker et al (5) was used for these calculations and the reader is referred to this work for more details.

SEWRPC has estimated that approximately 490×10^6 L/yr of gasoline is consumed in the Menomonee River Watershed. A telephone poll of service stations by members of the Water Chemistry Program indicates that the ratio of leaded to non-leaded gasoline sold in 1978 is approximately 40:60. Huntzicker et al (5) indicate that leaded gasolines contain an average of 0.56 g/L lead and that the non-leaded amount is 0.01 g/L. This yields an average consumption rate of 110 Tonnes/yr in the Menomonee River Watershed.

The model of Huntzicker et al (5) indicates that the fate of this lead is as follows: a. 27.5 Tonnes/yr remains in the cars (in the oil, oil filter

and exhaust system), b. 82.5 Tonnes/yr is exhausted to the atmosphere, c. of this 82.5 Tonnes/yr, 47 Tonnes/yr is deposited as large particulate matter within a few meters of the vehicles (near deposition), d. the remaining lead (35 Tonnes/yr) is available for long distance transport.

If one assumes a mass mean emission height of 1 to 5 m and an average windspeed of 7.5 km/hr 50%, i.e., 17.5 Tonnes Pb/yr would deposit within 1 to 8 km of the vehicles indicating that < 17.5 Tonnes/yr (21%) of the 82.5 Tonnes/yr emitted could leave the near vicinity of the Watershed.

Finally, a total lead deposition to the Watershed, i.e. lead produced outside added to that produced inside the Watershed can be calculated. From the previous sections it follows that $14 + \geq 65$ Tonnes/yr or ≥ 79 Tonnes Pb/yr deposit on the Watershed.

Delivery

From the investigations of Benninger et al (6) it is evident that lead is sequestered by soil and particulate matter in the river. Hence, significant dissolved concentrations do not occur in river water. Atmospherically-derived lead would not be expected to reach the river unless it was deposited on an impervious surface. Approximately 20% of the Watershed is impervious (roads, roofs, etc.). During the winter months, when the ground is snow covered and frozen, the extent of surface imperviousness is taken to be 100%. Using these assumptions it can be shown that 40% of the deposited lead from distant sources reaches the river. This is probably an overestimation since many impervious surfaces are not connected to channels. Further, since most of the lead will associate with particulate matter in the river, a very small fraction of the atmospheric lead reaches Lake Michigan.

However, locally high concentrations of lead probably occur. Most of the lead emitted in the Watershed is deposited on or near impervious surfaces so that lead concentrations in street runoff can be extremely high.

REFERENCES - II

1. Andren, A. W., S. Eisenreich, F. Elder, T. Murphy, M. Sanderson and R. J. Vet. Atmospheric Loading to Great Lakes. Special Report to International Joint Commission, Windsor, Ontario, Canada, 1978. 17 pp.
2. Hudson, J. L., J. J. Stukel and R. L. Solomon. Measurement of the Ambient Lead Concentration in the Vicinity of Urbana-Champaign, Illinois. Atmospheric Environment 9:1000-1006, 1975.
3. Habibi, K. Characterization of Particulate Lead in Vehicle Exhaust-- Experimental Techniques. Environ. Sci. Technol. 4(3):239-248, 1970.
4. Habibi, K. Characterization of Particulate Material in Vehicle Exhaust. Environ. Sci. Technol. 7(3):223-234, 1973.
5. Huntzicker, J. J., S. K. Friedlander and C. I. Davidson. Material Balance for Automobile-Emitted Lead in Los Angeles Basin. Environ. Sci. Technol. 9(5):448-457, 1975.
6. Benninger, L. K., D. M. Lewis and K. K. Turekian. The Use of Natural Pb-210 as a Heavy Metal Tracer in the River-Estuarine System. In: Marine Chemistry in the Coastal Environment, T. M. Church, ed. Am. Chem. Soc., Washington, D.C., Am. Chem. Soc. Symp. Ser. 18, 1975, pp. 201-210.

PART III
LEAD DEPOSITION TO LAKE MICHIGAN

by

T. R. STOLZENBURG
A. W. ANDREN

ABSTRACT

A model is used to determine lead flux to Lake Michigan by dry processes given certain average meteorological conditions and a suspended lead concentration of $0.5 \mu\text{g}/\text{m}^3$.

CONTENTS - PART III

Title Page	III-1
Abstract	III-11
Contents	III-111
Table	III-iv
III-1. Introduction	III-1
III-2. Conclusions.	III-2
III-3. Calculations and Discussion	III-3
References	III-7

TABLE

<u>Number</u>		<u>Page</u>
III-1	Dry deposition of atmospheric lead to Lake Michigan from Milwaukee, Wisconsin, November 1, 1976 to April 28, 1977 . . .	III-5

III-1. INTRODUCTION

Although only a small portion of the lead deposited on the Watershed from the atmosphere reaches Lake Michigan, particulate lead from automotive exhausts can enter the lake directly from the atmosphere. It is possible to treat metropolitan Milwaukee as an area source for lead and use a model such as the one presented by Gatz (1) to determine lead inputs to the lake given certain average meteorological conditions. These calculations were made in an effort to estimate the lead contribution from air over Milwaukee to that of total lake loading.

III-2. CONCLUSIONS

Model calculations suggest that, during the cold months (November to April), approximately 40 Tonnes of lead are deposited on Lake Michigan from Milwaukee by dry processes. Based on other estimates in the literature, this value represents 3% of the total atmospheric lead entering the lake each year.

III-3. CALCULATIONS AND DISCUSSION

The Menomonee River Watershed acts as a source of atmospheric lead since it has a relatively higher traffic density than the surrounding countryside. Prevailing westerly-winds carry lead aerosols over Lake Michigan. Lead aerosols have been shown to have a mass mean diameter of $0.4 \mu\text{m}$ (2). Data from Cawse (3) as compiled by Gatz (1), indicate that particles of this size have an average deposition velocity of 0.003 m/sec .

Thus, it is possible to estimate the amount of lead deposited by impaction in the lake from the area source designated as metropolitan Milwaukee. Gatz (1) introduced a mathematical model which can be used to calculate the pollutant contribution from the urbanized south shore of Lake Michigan. A modified version of this method has been developed here and a discussion of the input parameters to the model follows:

Deposition rate for a given particle is given by the general equation:

$$D = C \cdot V_d \quad \text{Eq. (1)}$$

where D is deposition rate in $\text{g/m}^2\text{-sec}$
 C is concentration of element near surface
in g/m^3 and
 V_d is deposition velocity in m/sec

The value to be determined is deposition rate. In this case, C is a variable which decreases with downwind distance from the area source (Milwaukee), as turbulence disperses the aerosol laterally. The average deposition velocity for lead will be taken as 0.003 m/sec in this calculation, although it undoubtedly varies as a function of wind speed.

The lake surface was divided arbitrarily into 5° pie-shaped sectors radiating out from Milwaukee. For each sector, the change in C_θ with downwind distance from the city (x_θ) is described by the equation:

$$C_\theta = \frac{Q}{Lu_\theta \left[\frac{2\pi(x_\theta + \frac{72y}{2\pi})}{72} \right]} \quad \text{Eq. (2)}$$

where Q is source strength in g/sec ,
 L is mixing height in m ,
 u_θ is wind speed for sector θ in m/sec ,

y is diameter of area source in m and
 x_θ is downwind distance to far shore for sector θ in m.

The area source diameter is taken to be 20,000 m and the mixing height as 850 m (4). From a mid-city station the averages of the inverse hourly wind speeds for each sector have been calculated. Downwind distance is a simple measurement and source strength, Q, is obtained from:

$$Q = C_o uLy \quad \text{Eq. (3)}$$

where C_o is mean concentration in air passing through a vertical plane at the downwind boundary of the source in g/m^3 and
 u is the mean wind speed m/sec.

An appropriate value for C_o is $0.5 \times 10^{-6} \text{ g/m}^3$ (5). The mean wind speed for all wind directions was calculated to be 7.5 km/hr from the same mid-city station.

To determine deposition for a particular sector, Q is calculated, followed by substitution of Eq. (2) into Eq. (1). An integration across the 5° arc and along x_θ produces a simplified formula:

$$D_\theta = \frac{Q V_d x_\theta}{Lu_\theta} \quad \text{Eq. (4)}$$

Finally, deposition for the whole lake consists of a summation of all 33 sectors multiplied by the frequency of wind in each sector (f_θ). Thus,

$$\sum_1^{33} D_\theta f_\theta = \text{total lake deposition.} \quad \text{Eq. (5)}$$

The calculation has been performed for the winter months from November 1976 to April 1977 (Table III-1). This season is defined by the condition that air over the lake surface is warmer than air over the land. The reverse condition resists aerosol deposition since little vertical mixing can occur over the lake surface. Gatz (1) suggests that summertime deposition is minimal. Hence, wind and mixing height values used in these calculations are averages for the cold months.

As the aerosol is transported to the far shore, continuous deposition depletes the suspended load. Therefore C_θ varies accordingly but is not accounted for by this model. A simple calculation shows that, in most cases, only a small fraction of the suspended load is lost ($\sim 8\%$). However, when wind speed is low and a long fetch is present, depletion can be significant. The hourly wind data suggests that such episodes occurred and deposition was over-estimated. However, the low average depletion indicates that such cases were rare.

It is interesting to compare values in Table III-1 with other deposition

Table III-1. Dry deposition of atmospheric lead to Lake Michigan from Milwaukee, Wisconsin, November 1, 1976 to April 28, 1977

Portion of Lake	Pb, Tonnes
Northern-two-thirds	54
Southern-one-third	69
Total	123

figures published in the literature. Andren et al (6) estimate that 1300 Tonnes of lead annually enter Lake Michigan through the atmospheric route. The calculation here (excluding wet deposition) suggests that about 9% of that total originates from the urban area around Milwaukee. The total contribution by Milwaukee may easily double if rain and snow were considered. Hence the total contribution from Milwaukee may be as high as 18%.

Gatz (1) estimated that 200 Tonnes of lead enters the lake annually from Chicago and northwest Indiana by wet and dry processes. At first glance this result appears inconsistent since the southern shore represents a much larger source strength than Milwaukee. However, the larger pollutant load is balanced by a lower frequency of offshore winds. Overall, Chicago and northwest Indiana represent a source strength almost five times as large as metropolitan Milwaukee, and yet the south shore contributes slightly less to Lake Michigan via the atmosphere.

REFERENCES - III

1. Gatz, D. F. Pollutant Aerosol Deposition into Southern Lake Michigan. Water, Air and Soil Pollution 5:239-251, 1975.
2. Rahn, K. The Chemical Composition of the Atmospheric Aerosol. Tech. Report, University of Rhode Island, Kingston, 1976.
3. Cawse, P. A. Report AERE-7769 Environmental and Medical Sciences Division, United Kingdom Atomic Energy Authority, Harwell, Oxfordshire. 1974.
4. Sievering, H. Dry Deposition Loading of Lake Michigan by Air-borne Particulate Matter. Water, Air and Soil Pollution 5:309-318, 1976
5. Schmidt, J. A. Selected Metals in Air Particulates Over Lake Michigan. University of Wisconsin-Madison, M.S. Thesis, 1977.
6. Andren, A. W., S. Eisenreich, F. Elder, T. Murphy, M. Sanderson and R. J. Vet. Atmospheric Loading to Great Lakes. Special Report to International Joint Commission, Windsor, Ontario, Canada, 1978. 17 pp.

PART IV
TOTAL PHOSPHORUS LOADING TO THE WATERSHED

by

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ABSTRACT

Wet deposition of phosphorus to the Watershed was calculated directly from measurements of phosphorus in rain. Dry deposition is calculated from an average suspended P concentration of $55 \mu\text{g}/\text{m}^3$ and a deposition velocity in the literature. Suspended P concentrations show marked seasonal trends at all stations.

CONTENTS - IV

Title Page	IV-1
Abstract	IV-11
Contents	IV-111
Figures	IV-1v
IV-1. Introduction	IV-1
IV-2. Conclusions	IV-2
IV-3. Methods and Procedures	IV-3
IV-4. Results and Discussion	IV-4
Rain Samples	IV-4
Wet Deposition	IV-4
Total Suspended Particulate Phosphorus	IV-5
Dry Deposition	IV-17
References	IV-18

FIGURES - IV

<u>Number</u>		<u>Page</u>
IV-1	Total suspended particulate phosphorus (TSSP) concentration at Falk Corporation site	IV-7
IV-2	Total suspended particulate phosphorus (TSSP) concentration at 70th Street site	IV-8
IV-3	Total suspended particulate phosphorus (TSSP) concentration at Appleton Avenue site	IV-9
IV-4	Total suspended particulate phosphorus (TSSP) concentration at River Lane site	IV-10
IV-5	Total suspended particulate phosphorus (TSSP) concentration at Donges Bay Road site	IV-11
IV-6	Mass concentration of phosphorus at Falk Corporation site . .	IV-12
IV-7	Mass concentration of phosphorus at 70th Street site	IV-13
IV-8	Mass concentration of phosphorus at Appleton Avenue site . . .	IV-14
IV-9	Mass concentration of phosphorus at River Lane site	IV-15
IV-10	Mass concentration of phosphorus at Donges Bay Road site . . .	IV-16

IV-1. INTRODUCTION

One of the key loading parameters designated for intensive study by the International Joint Commission was nutrients. Murphy and Doskey (1) concluded that 18% of the total phosphorus budget to Lake Michigan enters through precipitation directly on the lake surface. In a Lake Huron study, Delumyea and Petel (2) determined that dry deposition of phosphorus was probably of equal magnitude when compared to rain. A more recent study using bulk precipitation collectors showed that—in 1976 (a dry year)—16% of the total phosphorus entered Lake Michigan through the atmosphere (3). It is evident that as sewage treatment facilities implement nutrient removal techniques, atmospheric input of phosphorus to Lake Michigan will become the major source of this nutrient. Both Murphy and Doskey (1) and Delumyea and Petel (2) indicated that 40 to 50% of the incoming phosphorus is potentially available to the biota.

Having identified phosphorus as a critical parameter in terms of atmospheric transport, measurements were made on rain and suspended particulate air samples in the Menomonee River Watershed to determine the magnitude of deposition relative to loadings at the surface.

IV-2. CONCLUSIONS

Phosphorus concentrations in rain vary widely, from undetectable levels to well over 100 $\mu\text{g/L}$. A median value is in the range of 10 to 20 $\mu\text{g/L}$. Annual input of phosphorus to the Watershed by all forms of precipitation is at least 75 g/ha-yr.

Particulate phosphorus accounts for an average of 0.1% of the total suspended mass. The fraction is lowest in winter and highest in late summer. It is concluded that much of the phosphorus in air originates from continental dust.

Dry deposition of phosphorus is calculated to be 108 g/ha-yr. The sum of dry and wet deposition is somewhat lower than previous estimates.

IV-3. METHODS AND PROCEDURES

Rain and air sample collection and storage has been described previously. Immediate acidification of rain samples for trace metal analysis precluded measurement of available phosphorus. Only total phosphorus was analyzed on all samples.

Approximately 10% of the filter pad from air samples was digested in a 1:5 (v:v) mixture of H_2SO_4 and HNO_3 by the procedure described in American Public Health Assoc. (4). Rain samples were digested in an autoclave by a persulfate-sulfuric acid method (5). Color development for both types of samples involved the molybdate complex reduced to a blue color by ascorbic acid (5).

IV-4. RESULTS AND DISCUSSION

Rain

Phosphorus levels in rain varied widely. The range of concentration was from undetectable levels ($< 5 \mu\text{g/L}$) to over $100 \mu\text{g/L}$. A few extreme values tend to exaggerate the calculated means. Because of this it was thought that a median was a more appropriate expression of the average value. An overall median for all samples and stations is $10 \mu\text{g/L}$.

The question of which station exhibits the highest (or lowest) average phosphorus concentration does not have a clear-cut answer. For comparison purposes it is imperative to include only those events for which values exist for all stations, since P concentrations varied widely for different events. However, quite frequently one or more stations was inoperative for a particular event. This leaves very few events from which overall averages can be compared. Hence, the median concentrations from pairs of stations were compared in order to rank land use areas. The heavy industrial site (Falk Corporation) exhibited the lowest average phosphorus concentration. Appleton Avenue, representing a transition rural-urban station, had the highest median concentration relative to other land use areas. The rural, mixed rural, and residential areas were somewhere in between. One must immediately temper this conclusion by noting that phosphorus concentrations are probably a function of rainfall amount. The overall relationship also may show a seasonal dependence.

Wet Deposition

Loading calculations show that the minimum phosphorus loading does not occur at the Falk Corporation site since rain amounts tend to be heavier in the industrial valley. In addition, the maximum loading of phosphorus does not occur at Appleton Avenue since less rain was collected here than at most of the other stations for the events sampled. It appears that heavier rains have slightly lower phosphorus concentrations. Furthermore, it has been found that the concentrations of many trace constituents decrease during a rain event (6). Hence, loadings do not vary directly with amount of precipitation.

It is inappropriate to report phosphorus loadings by precipitation for single events since rainfall amounts vary dramatically across the Watershed. The sampler density was 1 per 5700 hectares, not nearly adequate enough to accurately measure event loading. However, yearly averages can be determined

with more confidence. For an average phosphorus concentration of 10 $\mu\text{g/L}$ and 51 cm rain, the annual input by rain would be 1738 kg or 51 g/ha.

Phosphorus content of snow was not measured, but is thought to contain as high a concentration of phosphorus, in terms of equivalent water volume, as rain (7). Since an average of 25 more centimeters equivalent water falls as snow, one would expect this to add at least 25 g/ha-yr phosphorus to the Watershed.

Another method for calculating total phosphorus deposition by rain is to sum the products of phosphorus concentrations and rain volumes for individual events through an entire year. Unfortunately, at no station is there a complete record. At the Falk Corporation site, where most events were collected and measured from 4/26/77 to 10/26/77, total phosphorus deposition was determined to be 46 g/ha. This is for a collected rain amount of 43 cm. At 70th St. (up to 10/20/77) the individual loadings added up to 43 g/ha-yr for a rain amount of 28 cm. Even though 70th St. received 32% less rain over the whole interval, the phosphorus loading dropped by only 7%. For comparative purposes, Murphy (8), measured phosphorus input at 250 g/ha-yr for a total rainfall of 71 cm in Chicago. Average total P concentrations in rain were 2.5 to 3 times higher than in this study.

The above measurements indicate that an average of 10 $\mu\text{g/L}$ phosphorus in rain may be a little low for calculating yearly input. If a precipitation weighted average concentration is used (1), the values are 11 $\mu\text{g/L}$ at the Falk site and 15 $\mu\text{g/L}$ at 70th St. These numbers represent the phosphorus concentrations if all rain samples were combined. These values compare favorably with the precipitation weighted concentration of 20 $\mu\text{g/L}$ reported for Illinois Beach State Park, 43 miles south of Milwaukee (1). Rain samples in the Murphy and Doskey (1) study were contaminated to a small degree by dry fallout.

For an average phosphorus in rain of 15 $\mu\text{g/L}$, and with rainfall amounts measured at 70th St., the phosphorus input is estimated for the spring seasons of 1975, 1976 and 1977. Rainfall totaled 18.5, 40.1 and 14.5 cm, respectively, for the spring seasons at this station. Hence, phosphorus deposition by rain was approximately 28 g/ha, 60 g/ha and 22 g/ha for these spring seasons.

Total Suspended Particulate Phosphorus

Measurements of total suspended particulate phosphorus (TSPP) were made with a greater degree of confidence because final sample solutions contained higher amounts of this material. The geometric mean concentration for all samples was 55 $\mu\text{g/m}^3$. The geometric mean was 1.1 mg/g, i.e., 0.1% of the total aerosol mass was phosphorus.

The ranking of land use areas by suspended phosphorus concentrations is much more clear-cut than by concentrations in rain. The heavy industrial site at Falk Corporation exhibited the highest suspended phosphorus load with an 86% frequency when the sampler was in operation. This trend is not unexpected, since for 93% of the time, the Falk Corporation site shows the

highest total suspended mass concentration. The linear correlation coefficient between total suspended mass and total suspended phosphorus being 0.878.

Ranking by phosphorus concentrations occurs in the following order 29% of the time during the sampling periods when all five stations were operating: Falk Corporation > 70th Street > Appleton Avenue > River Lane > Donges Bay Rd. This ranking is also the one most frequently observed for total suspended particulates. A major deviation from the above trend is the occurrence of relatively lower values at 70th Street compared to either Appleton Avenue or River Lane. The frequency of this observation is 43% of the samples.

Figures IV-1 to IV-5 exhibit the same chronological trend of TSPP for each station. Invariably, each plot indicates a relatively low concentration of suspended phosphorus during the period of early December, 1976 through mid-February, 1977. This strongly suggests that a major fraction of the suspended particulate phosphorus arises from continental dust, an aerosol source which is snow covered and frozen during this period.

Figure IV-6 to IV-10 show the mass concentration of phosphorus over time for each station; early February, 1977 undoubtedly marks a minimum. The trend appears to be upward through mid-August, and is especially evident in Figs. IV-9 and IV-10. Phosphorus accounts for an increasing percentage of the TSP as the year wears on, although at most, this value is 0.25%.

What is not immediately evident from the graphs, is the relationship between stations. The heavy industrial site generally exhibits a higher phosphorus fraction than either the mixed-rural or rural sites. This trend is reversed from mid-July through mid-August, when heavy rains occurred during or just preceding sampling periods. It is proposed therefore that suspendable street dust has a relatively high phosphorus content. This potential aerosol is either washed into the sewers or prevented from being suspended by heavy rains.

Sartor et al (9) found that street dust in the fraction < 43 μ m particle size contained 7.5 mg/g P. This amount is 7.5 times greater than the average phosphorus concentration in aerosols over the Menomonee River Watershed. In general, the phosphorus fraction in bulk soil also possesses a lower concentration than street dust. Buckman and Brady (10) report a range of 0.1 to 2 mg/g and Murphy (8) estimates the soil concentration at 0.42 mg/g. However, one expects to find higher concentrations for fertilized, agricultural soils and in certain industrial emissions, e.g., from iron and steel manufacturing (8). The suspended solids in the Menomonee River, which include urban and agricultural runoff, contain about 1.7 mg/g P (11). This value is calculated from the total loadings to Lake Michigan for 1975 and 1976 from both suspended solids and particulate phosphorus.

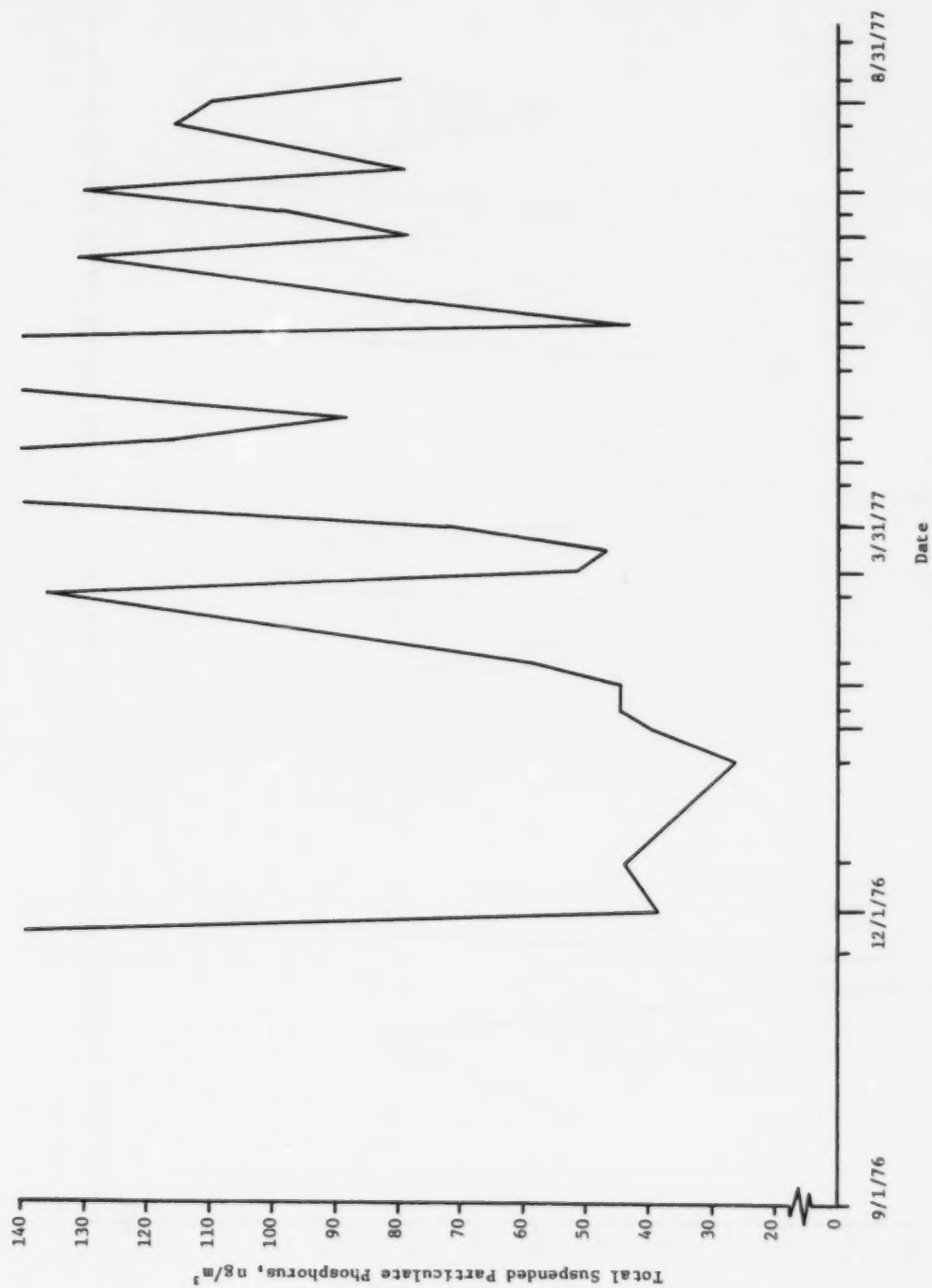


Fig. IV-1. Total phosphorus concentration at Falk Corporation site.

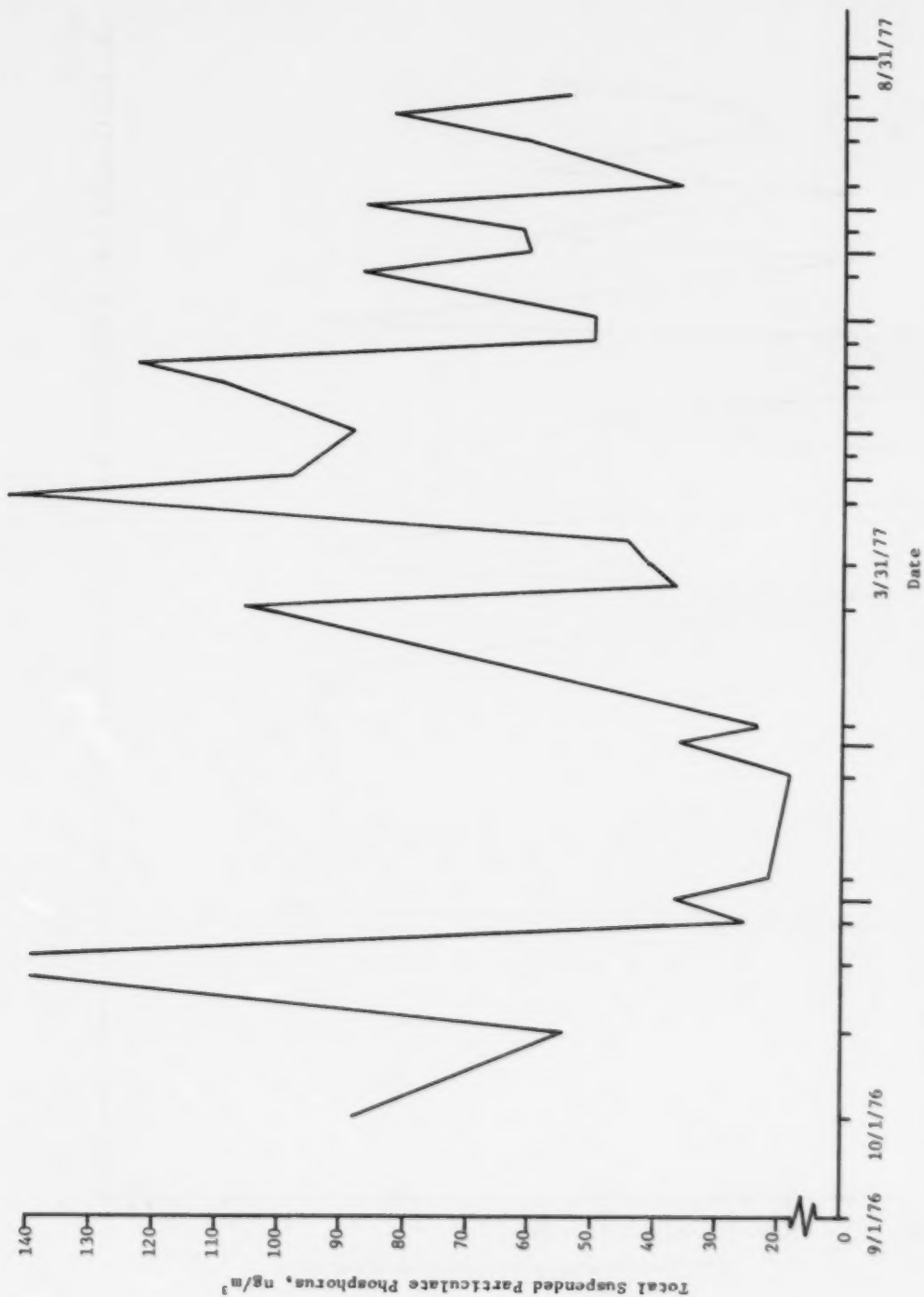


Fig. IV-2. Total phosphorus concentration at 70th Street site.

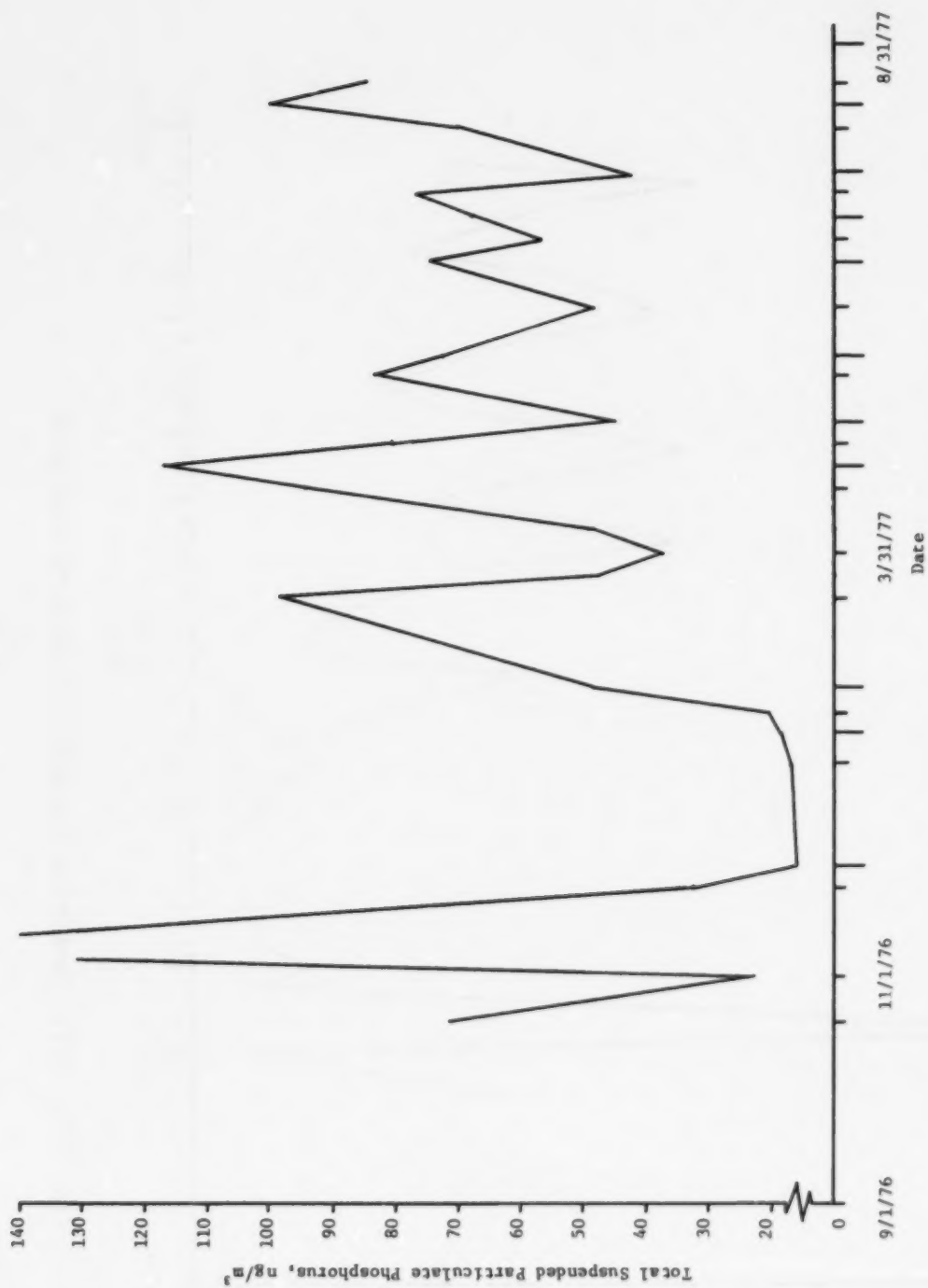


Fig. IV-3. Total phosphorus concentration at Appleton Avenue site.

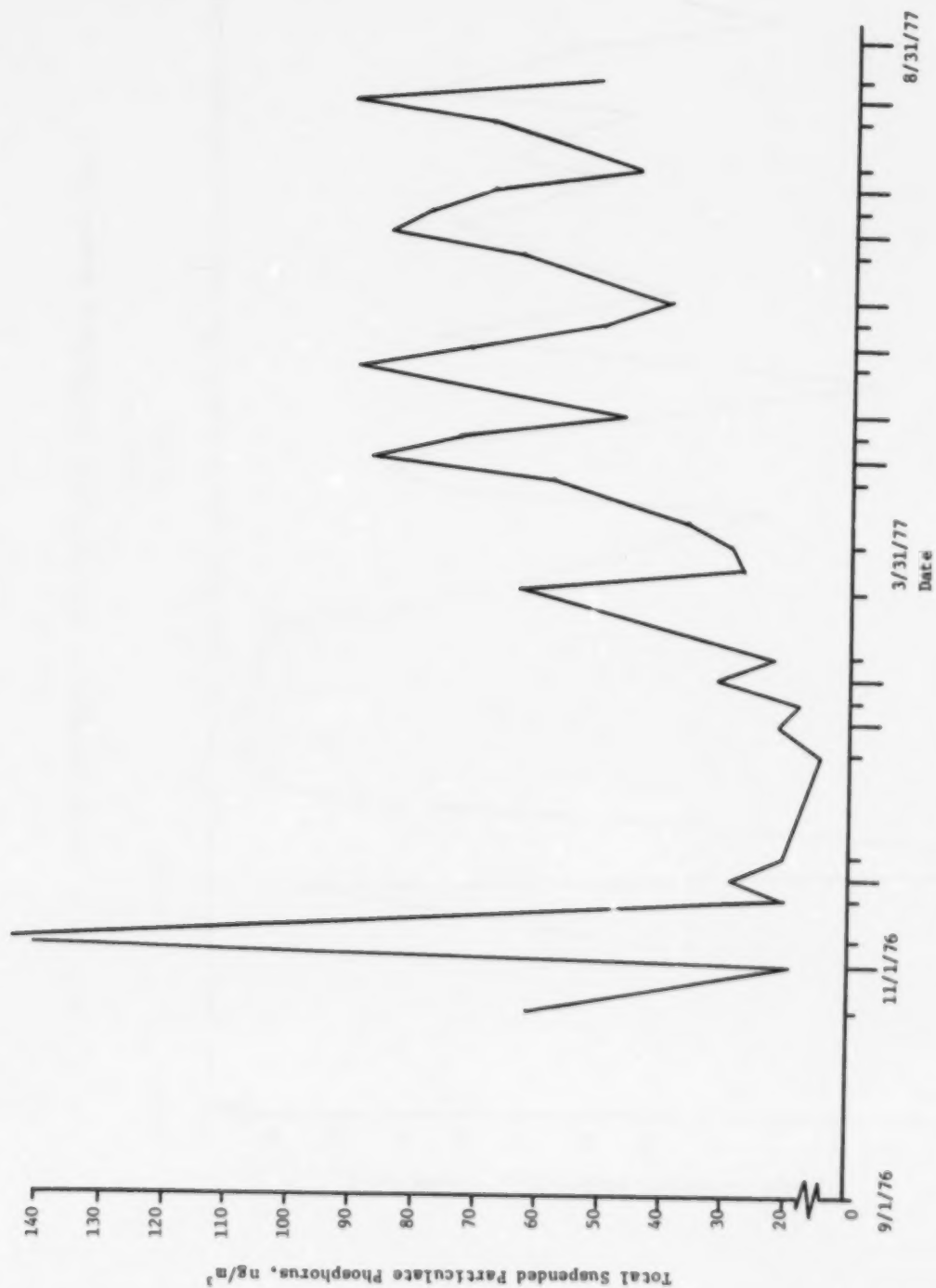


Fig. IV-4. Total phosphorus concentration at River Lane site.

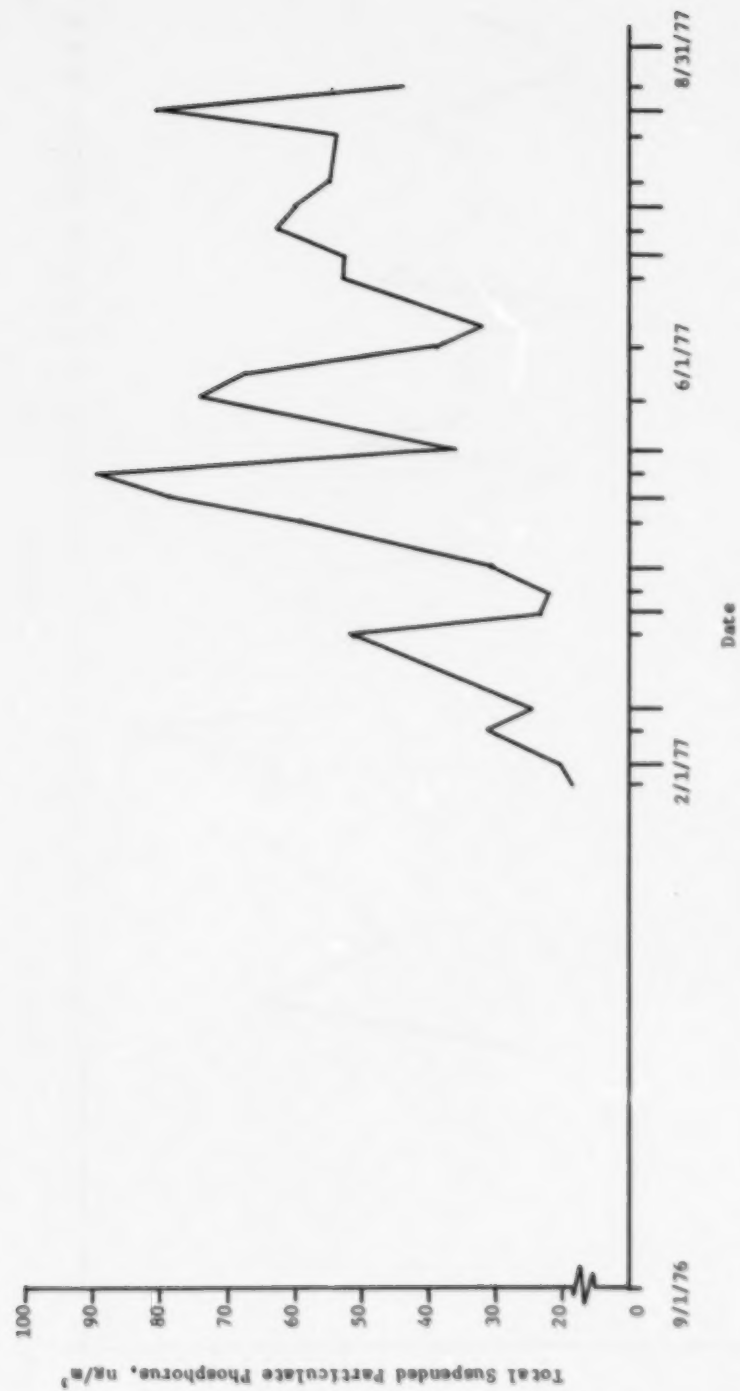


Fig. IV-5. Total phosphorus concentration at Donges Bay Road site.

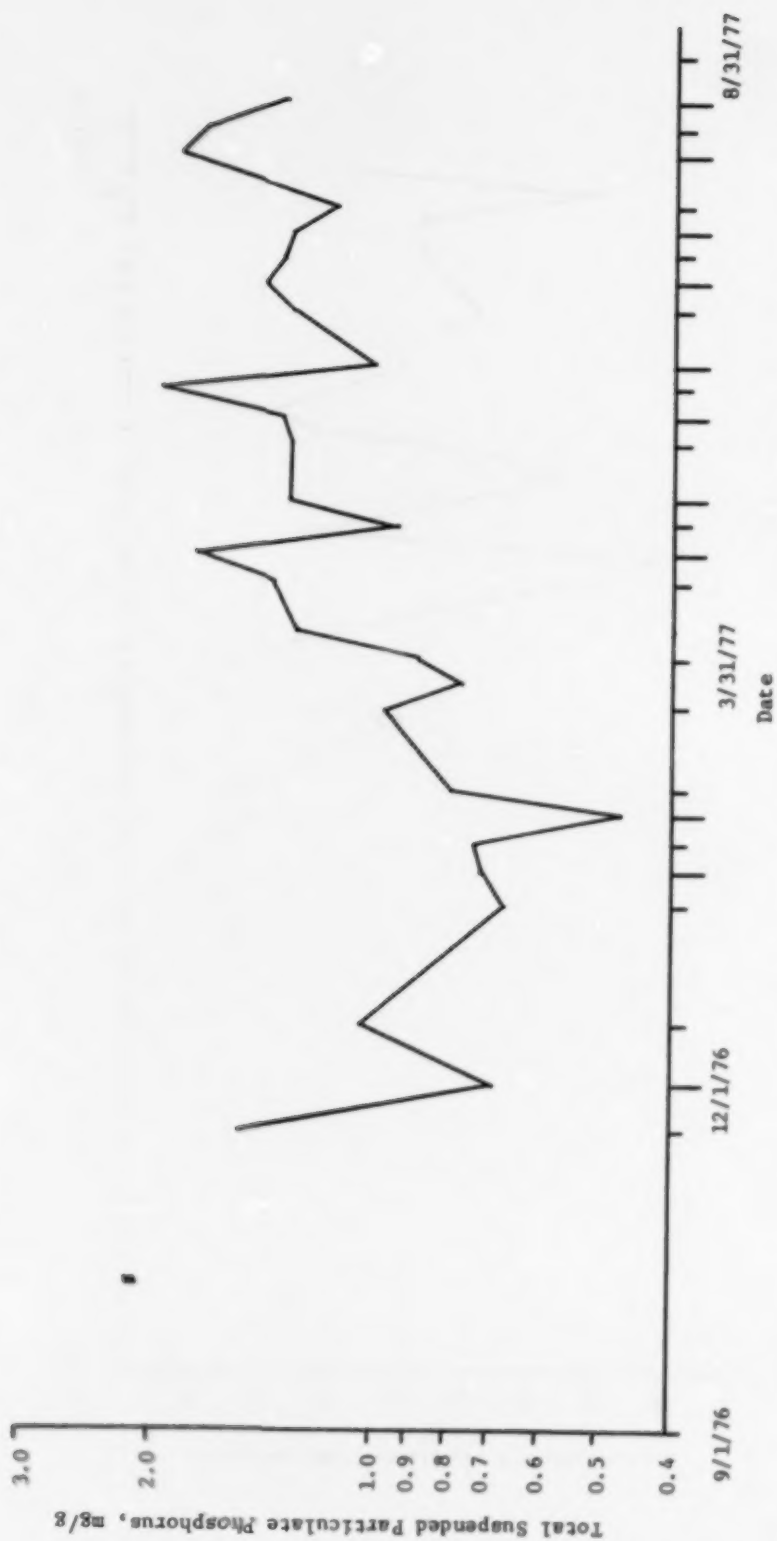


Fig. IV-6. Mass concentration of phosphorus at Falk Corporation site.

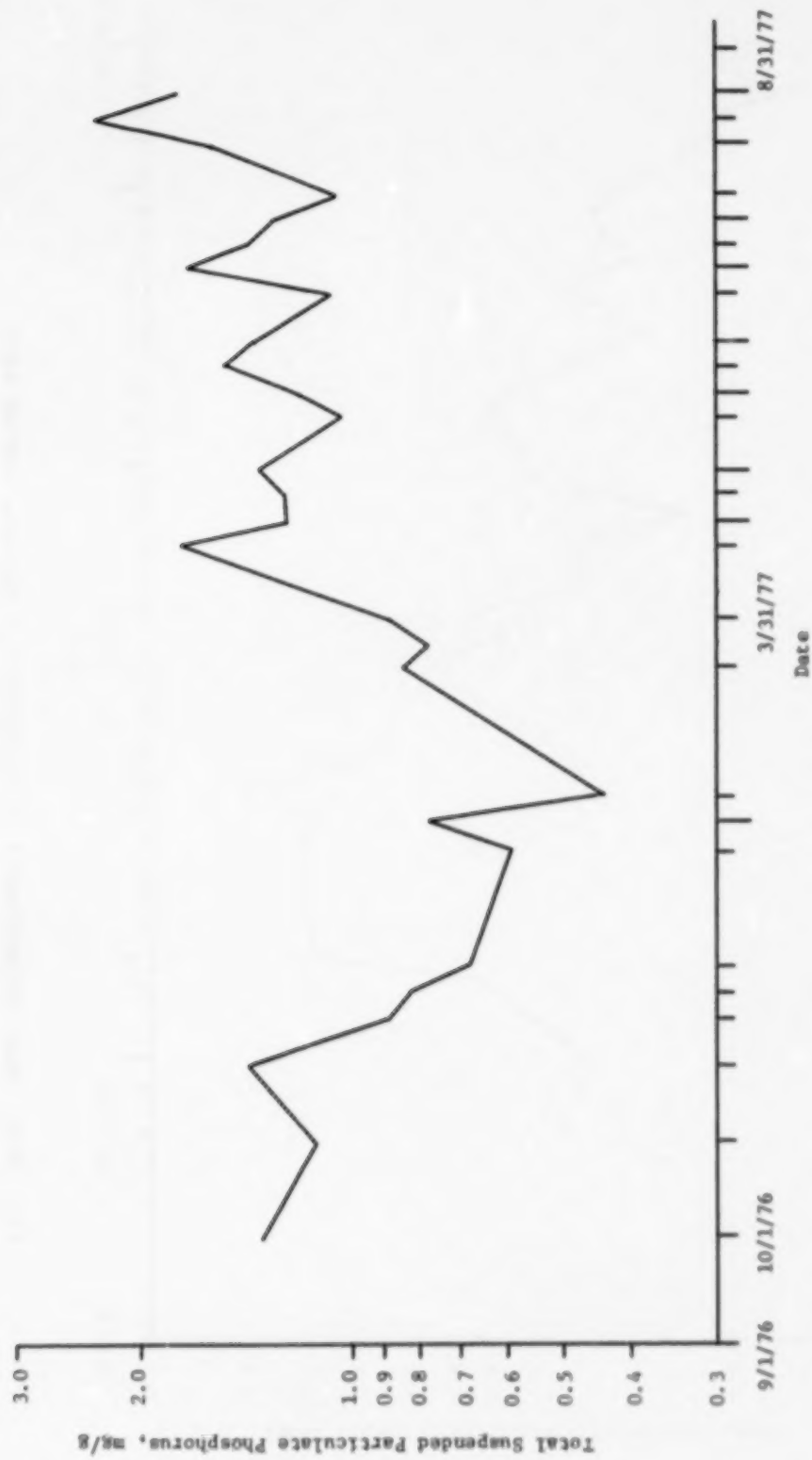


Fig. IV-7. Mass concentration of phosphorus at 70th Street site.



Fig. IV-8. Mass concentration of phosphorus at Appleton Avenue site.

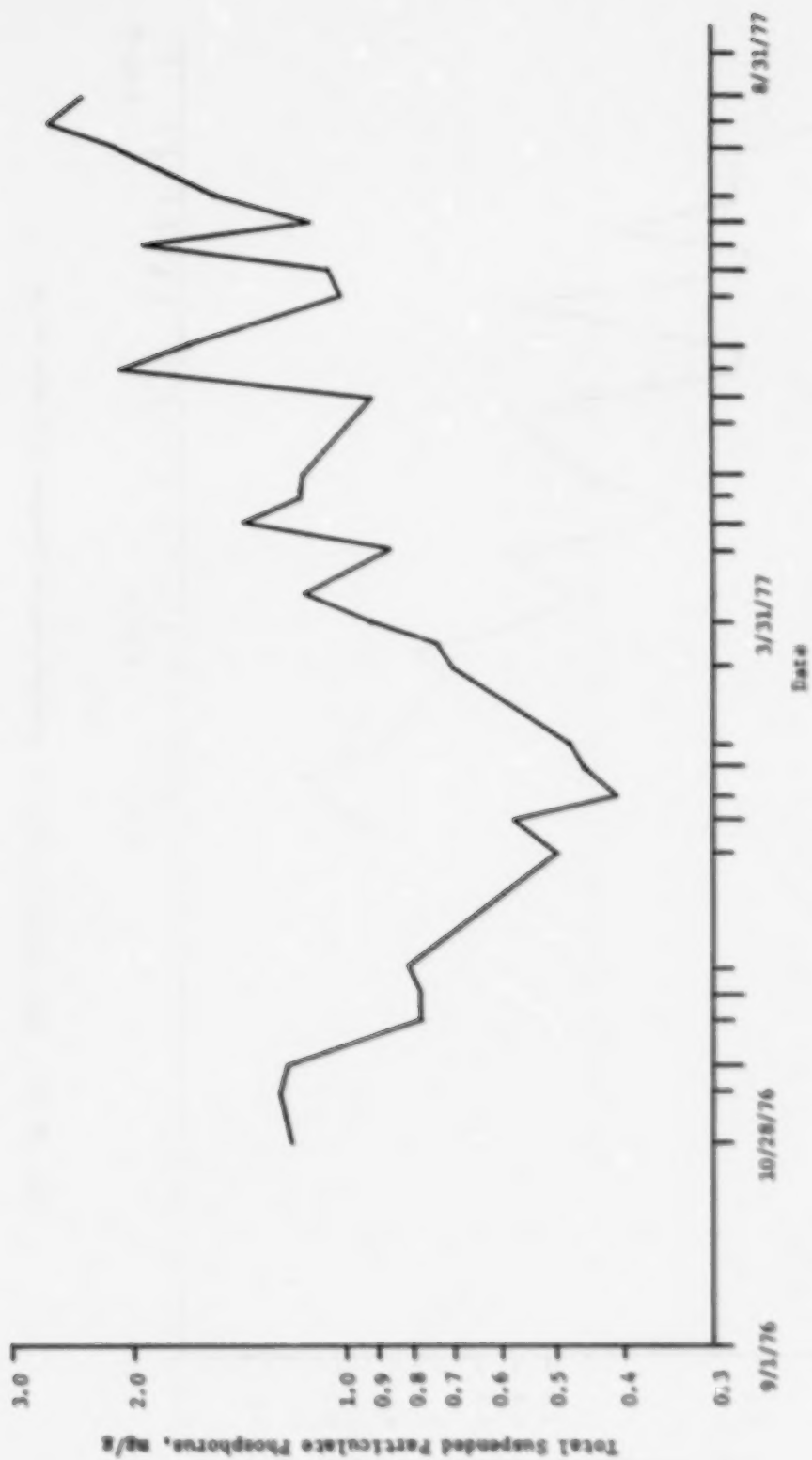
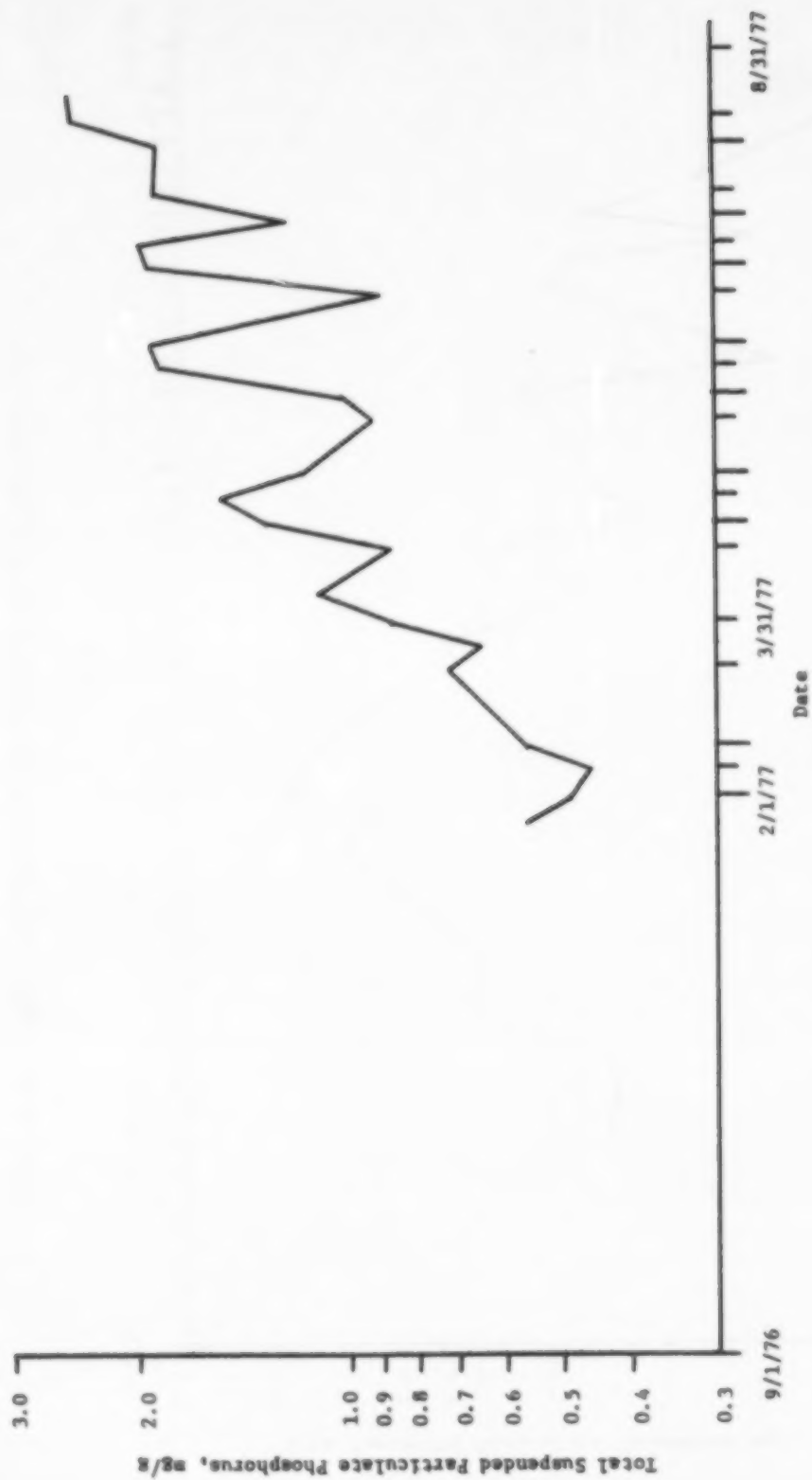


Fig. IV-9. Mass concentration of phosphorus at River Lane site.



Dry Deposition

Atmospheric loadings by dry deposition can be estimated from a knowledge of the suspended particulate phosphorus concentration and the size range with which most of the phosphorus mass is associated. The mass-particle size function of phosphorus is bimodal, corresponding to the two major emission sources, soil dust and combustion processes (2,8).

Delumyea and Petel (2) made detailed size distribution measurements around Lake Huron. The mass mean diameter for phosphorus containing particles was determined to be 1 μm . The calculated deposition velocity from the compiled data of Gatz (12) would approximate 0.5 cm/sec. The field data from the Lake Huron study indicated a deposition velocity of 0.6 cm/sec. The average phosphorus concentration over the Menomonee River Watershed was estimated at 55 $\mu\text{g}/\text{m}^3$. Thus, deposition for the area can be calculated using the expression described in Part III.

$$D = V_d \cdot C \quad \text{Eq. (1)}$$

Dry deposition rate to the Menomonee River Watershed is thus 108 g/ha-yr or 3.46×10^3 kg/yr for the entire area. Phosphorus concentrations and deposition rate vary seasonally. It is thus evident that the above values should only be considered approximate.

Bulk precipitation samplers in Milwaukee indicated an average loading rate of phosphorus at 372 g/ha-yr (3). This value is somewhat greater than the sum of loading estimates made in this study for rain, snow and dry deposition, i.e. $50 + 25 + 108$ g/ha-yr. Using 15 $\mu\text{g}/\text{L}$ as the best estimate of the average phosphorus concentration in precipitation, the total loading estimate for the Menomonee River Watershed would be increased to 220 g/ha-yr.

Intuitively, one might speculate that the virtual deposition surface formed by the open end of a cylindrical bulk collector is an underestimate of the actual surface area available for deposition by impaction. Hence, further investigations may reveal that bulk collectors overestimate the dry deposition rate.

REFERENCES - IV

1. Murphy, T. J. and P. B. Doskey. Inputs of Phosphorus from Precipitation to Lake Michigan. U.S. Environmental Protection Agency Report No. EPA-600/3-75-005, Grosse Ile, Michigan. 1975.
2. Delumyea, R. G. and R. L. Petel. Atmospheric Inputs of Phosphorus to Southern Lake Huron. U.S. Environmental Protection Agency Report No. EPA-600/3-75-038, Ann Arbor, Michigan. 1977.
3. Eisenreich, S. J., P. J. Emmling and A. M. Beeton. Atmospheric Loading of Phosphorus and Other Chemicals to Lake Michigan. J. Great Lakes Res. 3(3-4):291-304, 1977.
4. American Public Health Assoc. Standard Methods for Examination of Water and Wastewater, 13th ed. APHA, Washington, D.C. 1971.
5. U.S. Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. U.S. Environmental Protection Agency Report No. EPA-625/6-74-003, Environmental Research Center, Cincinnati, Ohio. 1976 (Revised).
6. Ronneau, C., J. Cara, J. L. Navarre and P. Priest. An Automatic Sequential Rain Sampler. Water, Air and Soil Pollution 9:171-176, 1978.
7. Shiomi, M. T. and K. W. Kuntz. Great Lakes Precipitation Chemistry: Part 1, Lake Ontario Basin. Proc. 16th Conf. on Great Lakes Research, International Assoc. of Great Lakes Research, pp. 581-602. 1973.
8. Murphy, T. J.. Sources of Phosphorus Inputs from the Atmosphere and Their Significance to Oligotrophic Lakes. Water Resources Center, University of Illinois, Urbana, Research Report No. 92. 1974.
9. Sartor, J. D., G. B. Boyd and F. J. Agardi. Water Pollution Aspects of Street Surface Contaminants. J. Water Pollution Control Fed. 46:458-467, 1974.
10. Buckman, H. O. and N. C. Brady. The Nature and Properties of Soils. Collier-Macmillan Ltd., London, 1971.
11. Sonzogni, W. C., T. J. Monteith, W. N. Back and V. G. Hughes. United States Great Lakes Tributary Loadings. PLUARG Technical Report to Task D, Ann Arbor, Michigan. 1978.
12. Gatz, D. T. Pollutant Aerosol Deposition into Southern Lake Michigan. Water, Air and Soil Pollution 5:239-251, 1975.

PART V

EVALUATION OF SOURCES

by

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ABSTRACT

A model utilizing multivariate regression analysis is used to predict major emission sources contributing to the suspended dust in the Menomonee River airshed. This source reconciliation model is sensitive to changes in ambient aerosol composition caused by inputs of various emission sources.

CONTENTS-PART V

Title Page.....	V-1
Abstract.....	V-11
Contents.....	V-111
Tables.....	V-1v
V-1. Introduction.....	V-1
V-2. Conclusions.....	V-2
V-3. Evaluation of Sources.....	V-3
References.....	V-18
Appendix	
V-A. Soil Analyses.....	V-19

TABLES

<u>Number</u>		<u>Page</u>
V-1	Source profiles.....	V-7
V-2	Fit heavy industrial ambient aerosol with 8 emission sources.....	V-9
V-3	Fit heavy industrial ambient aerosol with 8 modified emission sources.....	V-10
V-4	Fit heavy industrial ambient aerosol with 7 modified emission sources.....	V-12
V-5	Fit heavy industrial ambient aerosol with 6 emission sources.....	V-13
V-6	Fit rural ambient aerosol with 7 emission sources.....	V-14
V-7	Fit rural ambient aerosol with 7 emission sources weight Q_i by 1/10.....	V-15
V-8	Fit rural, winter ambient aerosol with 7 emission sources...	V-17
V-A-1	Metal analyses of agricultural soil samples from the Menomonee River Watershed.....	V-19
V-A-2	Metal analyses of construction site soil samples from the Menomonee River Watershed.....	V-20

V-1. INTRODUCTION

Government regulatory agencies are coming under increasing pressure to provide evidence that those industries being regulated can be held responsible for the levels of ambient aerosols measured. For this reason, the development of accurate and convenient source reconciliation methods is imperative.

The method presented here employs routine bulk analysis of ambient aerosols by atomic absorption spectrometry. Given the elemental composition of emission sources and ambient aerosols, successful source reconciliation is achievable by multivariate regression analysis.

V-2. CONCLUSIONS

The source reconciliation model presented here is generally applicable at any atmospheric monitoring site. Accurate ambient elemental measurements needed for input parameters to the computer program are routinely attainable by high volume air sampling and atomic absorption analysis.

Results of this study indicate the model is sensitive to changes in ambient aerosol composition caused by the relative inputs of various emission sources. The composition of ambient aerosol in a heavy industrial land use clearly reflects contributions of local emission sources. The relative contribution of these anthropogenic emission sources decreases dramatically over a distance of 15 km in a direction generally perpendicular to the prevailing wind.

V-3. EVALUATION OF SOURCES

Multivariate regression analysis was used to determine the major emission sources contributing to the observed suspended dust in the Menomonee River airshed. The method of Mayrsohn and Crabtree (1) is presented below. A slight modification was introduced to improve the fitting qualities of the model.

Ideally, one would like to know the actual fraction of measured aerosol contributed by each source. This fraction is known as a source coefficient. The mathematical expression of the source coefficient is given in Eq. (1).

$$m_x = \sum_j^n c_j (\alpha_{xj}) (p_{xj}) \quad \text{Eq. (1)}$$

where

c_j is source coefficient; fraction of aerosol contributed by source j
 p_{xj} is fraction of source j that is element x
 m_x is fraction of aerosol that is element x
 α_{xj} is coefficient of fractionation

For a given element, both particle size distribution and distance travelled influence α_{xj} . It is impossible to assign a value to α_{xj} , it is set equal to 1. An objection to this would be legitimate, but at present no mathematical method has been developed to describe the fractionation process. The fraction, m_x , of the aerosol that is element x is a measured value. One must either measure p_{xj} or take a value from the literature. The value to be calculated is c_j .

A simple case occurs when the number of elements equals the number of sources. Three equations are solved simultaneously for three unknowns. For instance:

Example 1.	Elements - x,y,z	Sources - j,k,l
	$c_j(p_{xj}) + c_k(p_{xk}) + c_l(p_{xl}) = m_x$	
	$c_j(p_{yj}) + c_k(p_{yk}) + c_l(p_{yl}) = m_y$	
	$c_j(p_{zj}) + c_k(p_{zk}) + c_l(p_{zl}) = m_z$	

Normally the elements considered are not present in significant quantities in all the sources. To obtain a source coefficient for a source, a tracer element is assigned. This element would have no other major sources (e.g., lead in automobile exhaust). Assuming that all lead in aerosol samples originates from leaded gasoline, the source coefficient calculation is simplified. A single equation is needed for the determination in the following example.

Example 2. $P_{Pb,k}$, $P_{Pb,l}$, $P_{Pb,o}$, ... are negligible

$$m_{Pb} = P_{Pb,auto} (c_{auto})$$

therefore,

$$\text{Using typical values: } P_{Pb,auto} = 0.40$$

$$m_{Pb} = 0.003$$

$$\begin{aligned} c_{auto} &= m_{Pb} \div P_{Pb,auto} \\ &= 0.003 \div 0.40 = 0.0075 \end{aligned}$$

With slight modifications the calculations can still be handled readily. For instance, lead may have two sources, one of which is fuel oil combustion, the other auto exhaust. However, if a suitable tracer can be found for the fuel oil source, both source coefficients can be determined.

Example 3.

Step A. Vanadium is known to be a good tracer for fuel oil.

$$c_{fuel\ oil} = m_V \div P_{V,fuel\ oil}$$

$$\text{For typical values: } P_{V,fuel\ oil} = 2.5$$

$$m_V = 0.04$$

$$c_{fuel\ oil} = 0.04 \div 2.5 = 0.016$$

Step B. With the source coefficient for fuel oil, one can determine the amount of lead in the measured aerosol contributed by fuel oil combustion:

$$\begin{aligned} m_{Pb,fuel\ oil} &= P_{Pb,fuel\ oil} (c_{fuel\ oil}) \\ &= 0.04 (0.016) \end{aligned}$$

$$m_{Pb,fuel\ oil} = 0.00064$$

Step C. By subtracting lead contributed by fuel oil from the total lead measured, one obtains that amount contributed by auto exhaust:

$$\begin{aligned} m_{Pb,auto} &= m_{Pb} - m_{Pb,fuel\ oil} \\ &= 0.003 - 0.00064 = 0.00236 \end{aligned}$$

Step D. The source coefficient for auto exhaust is calculated knowing that $P_{Pb,auto} = 0.40$

$$\begin{aligned} c_{auto} &= m_{Pb,auto} \div P_{Pb,auto} \\ &= 0.00236 \div 0.40 = 0.0059 \end{aligned}$$

Still more complications prevent utilization of these simplified formulae. Some sources do not have tracer elements which can readily be identified. Most of the time, the number of elements analyzed is greater than the number of sources considered. In essence, there exists more data than necessary to solve the equations directly. However, there is some error in all elemental concentration measurements. It would thus be useful to have as much of the data as possible to obtain an average calculation of the source coefficients.

The method of multivariate regression analysis for source reconciliation embodies this concept. In simple terms, the set of source coefficients is computed which will yield an aerosol composition that most closely resembles the measured profile. A computer program is used so that many sources and elements can be accommodated.

When using many elements and sources, the elemental composition of each source, the measured aerosol profile and the set of source coefficients can be treated as matrices. Henceforth, the composition of a source shall be named source profile, and capital letters will denote matrices.

P is the source profile
M is the measured aerosol profile
C is the set of source coefficients
e is the number of elements
n is the number of sources

Equation (1) can be rewritten in matrix form:

$$M = P \cdot C$$

where the α factors have been deleted.

Rewriting Example 1.:

$$\begin{bmatrix} p_{xj} & p_{xk} & p_{xl} \\ p_{yj} & p_{yk} & p_{yl} \\ p_{zj} & p_{zk} & p_{zl} \end{bmatrix} \cdot \begin{bmatrix} c_j \\ c_k \\ c_l \end{bmatrix} = \begin{bmatrix} m_x \\ m_y \\ m_z \end{bmatrix}$$

P C = M

In the case of multivariate analysis of real data, P and M are measured and an approximation of C is computed.

Since analytical errors are inherent in both P and M, and the number of elements is greater than the number of sources, an exact solution, C, for the equation $P \cdot C = M$ does not exist. However, for any approximation of C, we can compute a source profile, E, where $E = P \cdot C$. The best approximation of C is found by minimizing $D = E - M$, the difference between the computed and measured profiles.

The calculation is written in more complete form below. If individual elements of matrices are denoted by small case letters, then:

$$d_y = \left[\sum_{j=1}^n c_j p_{yj} \right] - m_y \quad \text{Eq. (2)}$$

The elements of D are now squared and summed to yield a lengthy function not shown here:

$$\left[\sum_{y=1}^e (d_y)^2 \right] = f(c_1, c_2, c_3, \dots, c_n) \quad \text{Eq. (3)}$$

A judicious selection of source coefficients will bring the calculated aerosol profile more or less close to the measured aerosol profile. An expression of this proximity is found in Eq. (4).

$$\left[\sum_{y=1}^e (d_y)^2 + (e-1) \right]^{1/2} \quad \text{Eq. (4)}$$

This value will be termed the standard error of estimate, and is an index of fit.

The expression in Eq. (3) can be minimized by taking the partial derivative with respect to each c_j and setting it equal to zero. A solution of n simultaneous equations will yield a set of source coefficients which gives the closest approximation to the measured aerosol profile.

The first step in applying this model is to consider all major emission sources which may contribute significant fractions to the total aerosol in the watershed. In a previous source reconciliation study of Chicago aerosols, Gatz (2) accounted for contributions from 6 sources. For this study, 8 sources will initially be considered.

Source profiles for automotive exhaust, fuel oil fly ash and cement manufacturing were taken from Friedlander (3). The composition of municipal incineration emissions are reported in Greenberg et al. (4). Iron and steel manufacturing data is listed by Gatz (2). Coal burning emissions were taken from Klein et al. (5) and Andren and Lindberg (6).

Surface soil samples were collected from the watershed at a construction site and a tilled field. Windblown dust from bulk soil fractionates elements according to their preference for particle size. The fractionation factors, found by Miller et al. (7), were multiplied by the average elemental values measured in Menomonee Watershed soil to obtain the composition of soil dust. Appendix V-A lists individual and mean soil concentrations measured in soil samples. The source profiles used for the regression analysis are compiled in Table V-1.

The modification mentioned in the beginning of this section concerns weighting the ultimate fit to individual element differences.

The regression analysis of Mayrsohn and Crabtree (1) minimizes the sum of the squares of the absolute differences between measured and computed aerosol profiles. Evidently, for this study, the

Table V-1. Source profiles

Element	Coal fly ash (COAL)	Automotive emissions (AUTO)	Fuel oil ash (FOASH)	Cement manufacture (CEMENT)	Iron and steel manufacture (IR&ST)	Agricultural soil dust (ASOLID)	Construction soil dust (CSOILD)	Incineration emissions (INCIN)
Al	8.11	--	0.8	2.4	2.4	6.3	5.2	1.4
Ca	2.7	--	1.3	46.0	5.4	2.4	16.5	--
Cu	0.054	--	0.2	--	1.6	0.014	0.01	0.17
Fe	10.5	0.4	6.0	1.09	38.7	4.8	4.2	0.65
K	2.43	--	0.2	0.53	--	0.90	1.0	--
Hg	13.5	--	0.06	0.48	1.6	2.2	12.8	1.3
Mn	0.054	--	0.06	--	2.4	0.16	0.13	0.073
Na	1.08	--	5.0	0.4	--	0.80	0.47	8.2
Pb	0.054	40.0	0.07	--	--	0.003	0.003	8.1
Zn	0.54	0.14	0.02	--	1.8	0.012	0.0077	12.0

calculation would be most sensitive to aluminum, calcium and iron, whose concentrations are the highest in the aerosol profile. A proportional error in the computed zinc concentration would have a minimal influence on the overall fit. Therefore, correct determination of source coefficients is highly dependent on the accuracy and completeness of the major element data.

Although absolute concentrations are orders of magnitude lower, the measurement of the trace constituents (e.g. Mn and Zn) is as accurate as the major elements. It is contradictory to include many more elements in a source coefficient calculation in hopes of improving the approximation, and yet weighting the fit to only a few. Hence, the computer program in this study weights each element equally by dividing by the measured ambient concentration. In addition, more versatility was added by including an option to weight individual elements to any desired level. The following discussion illustrates the utility of multivariate regression analysis.

An ambient aerosol sample from the heavy industrial site in August was chosen for source reconciliation. Table V-2 shows the calculated fit with the 8 considered emission sources. The measured aerosol profile, expressed in percentage units, is the first of 4 columns. Both unweighted and weighted values will be shown in each case. The standard error is an expression of overall fit, a low number indicating similarity between computed and measured profiles.

Negative source coefficients indicate that some of the data is incomplete or inaccurate. The final column shows that potassium contributes most to the difference between measured and computed profiles. In fact, the aerosol contains much more potassium than is accounted for by the sources considered.

In reevaluating the emission source profiles, it was noted that Gatz (2) reports no potassium or sodium emissions from iron and steel manufacturing. However, Murphy (8) lists a sodium percentage from this source as 1.03%. It is likely that potassium is also emitted, but simply was not reported. There is no firm basis for calculating a potassium percentage, but a tentative value can be assigned by noting the sodium to potassium ratios in coal and cement. Potassium contents are generally higher in these sources, and hence a value of 1.5% potassium was chosen for iron and steel.

Utilizing the modified source profile for iron and steel, the regression analysis was run a second time (Table V-3). The sodium and potassium changes improved the overall fit, but the troublesome negative source coefficients still persisted. It is probable that some of the sources considered contribute very little mass to the total measured aerosol. The agricultural soil dust source exhibits the most negative source coefficient and was deleted on that basis. There is no mathematical justification for deleting an emission source with the most negative value. However, if the overall fit improves, there can be little argument in favor of retaining the source in question.

Table V-2. Fit heavy industrial ambient aerosol with 8 emission sources

SOURCE COEFFICIENTS

COAL	AUTO	FOASH	CEMENT	IR&ST	ASOILD	CSOILD	INCIN	SUM
.3816	.0310	.1027	.1371	.1097	-.2112	-.1025	-.0061	.4422

UW-MEA: UNWEIGHTED MEASURED AEROSOL PROFILE
 UW-COM: UNWEIGHTED COMPUTED AEROSOL PROFILE
 UW-RES: UNWEIGHTED RESIDUAL
 W-RES: WEIGHTED RESIDUAL

ELEMENT	UW-MEA	UW-COM	UW-RES	W-RES
AL	1.820000	1.896698	-.076698	-.042142
CA	5.820000	5.863515	-.043515	-.007477
CU	.230000	.211577	.018423	.080101
FE	5.730000	7.580120	-1.850120	-.322883
K	1.100000	.727853	.372147	.338315
MG	3.570000	3.614123	-.044123	-.012359
MN	.314000	.242374	.071626	.228107
NA	.733000	.713198	.019802	.027015
PB	1.220000	1.219011	.000989	.000811
ZN	.330000	.333143	-.003143	-.009523

STANDARD ERROR OF ESTIMATE -- INDEX OF FIT

.3741428

Table V-3. Fit heavy industrial ambient aerosol with 8 modified emission sources

SOURCE COEFFICIENTS

COAL	AUTO	FOASH	CEMENT	IR&ST	ASOILD	CSOILD	INCIN	SUM
.3029	.0307	.0799	.1127	.1157	-.1674	-.0282	-.0035	.4426

UW-MEA: UNWEIGHTED MEASURED AEROSOL PROFILE
 UW-COM: UNWEIGHTED COMPUTED AEROSOL PROFILE
 UW-RES: UNWEIGHTED RESIDUAL
 W-RES: WEIGHTED RESIDUAL

ELEMENT	UW-MEA	UW-COM	UW-RES	W-RES
AL	1.820000	1.862011	-.042011	-.023083
CA	5.820000	5.862090	-.042090	-.007232
CU	.230000	.214203	.015797	.068684
FE	5.730000	7.347329	-1.617329	-.282256
K	1.100000	.806329	.293671	.266974
MG	3.570000	3.598701	-.028701	-.008040
MN	.314000	.268086	.045914	.146223
NA	.733000	.714546	.018454	.025177
PB	1.220000	1.219129	.000871	.000714
ZN	.330000	.332890	-.002890	-.008757

STANDARD ERROR OF ESTIMATE -- INDEX OF FIT

.2986664

Table V-4 shows another improvement in fit by removing the agricultural soil dust source. In addition, all source coefficients are positive. The process could be ended here. However, the regression analysis allows us to remove any element(s) as long as the remaining number of elements exceeds the number of sources. Since iron and potassium contribute most to the overall error, they were deleted in Table V-5.

The questionable tactic of assigning a potassium concentration was thereby rendered inconsequential. Incineration emissions are clearly negligible ($< 0.5\%$). This source was deleted.

Table V-5 is the final reconciliation of emission sources for the heavy industrial site. The considered sources account for 53% of the total measured aerosol mass. Coal combustion, iron and steel manufacturing and soil dust from a construction site, together account for 36% of the total mass.

In a study by Draftz et al. (9) 90% of the particulate matter collected at most suburban Chicago sites was said to be concrete dust and automotive emissions. In this source reconciliation, the cement emission profile would represent concrete dust. Automotive emissions are also taken into account. Table V-5 shows that, at most, 8.5% of the total dust is due to vehicular activity, assuming that all cement emissions are actually via concrete ablation.

The reconciliation was then performed on the rural site aerosol from the same sampling period (Table V-6). The agricultural soil dust source appears to contribute to the rural aerosol. The major error is from copper. Copper cannot be deleted since the number of elements would then equal the number of sources. At this point, the versatility of weighting becomes evident. The dependence of the overall fit on copper can be reduced by a factor of 10.

Table V-7 is the final reconciliation of the rural aerosol after desensitizing the analysis to copper. The standard error of estimate is very low. Source coefficient calculations show a decrease in contribution from iron and steel by 10 times in the 15 km between Falk and Donges Bay. Auto emission contributions are decreased by more than a factor of 2, while coal combustion contributions went down 40%.

The results were expected. Anthropogenic emissions contribute a major fraction of the total measured dust in the industrial valley. The effect is, however, extremely localized in a north-south direction.

The accuracy of the computer program can be checked by two simple tests. In the past, automotive emissions have been successfully reconciled using a tracer element calculation (i.e. Pb). To confirm the computer calculated source coefficient of 0.0303 in Table V-5, the tracer determination was carried out in Eq. (5).

$$c_{\text{auto}} = m_{\text{Pb}} \div p_{\text{Pb, auto}} \quad \text{Eq. (5)}$$

$$= 1.22 \div 40 = 0.0305$$

Table V-4. Fit heavy industrial ambient aerosol with 7 modified emission sources

SOURCE COEFFICIENTS

COAL	AUTO	FOASH	CEMENT	IR&ST	CSOILD	INCN	SUM
.1496	.0295	.0693	.0712	.1152	.0835	.0031	.5213

UW-MEA: UNWEIGHTED MEASURED AEROSOL PROFILE
 UW-COM: UNWEIGHTED COMPUTED AEROSOL PROFILE
 UW-RES: UNWEIGHTED RESIDUAL
 W-RES: WEIGHTED RESIDUAL

ELEMENT	UW-MEA	UW-COM	UW-RES	W-RES
AL	1.820000	2.153997	-.333997	-.183515
CA	5.820000	5.766276	.053724	.009231
CU	.230000	.207540	.022460	.097652
FE	5.730000	6.884598	-1.154598	-.201500
K	1.100000	.671228	.428772	.389792
MG	3.570000	3.314306	.255694	.071623
MN	.314000	.299680	.014320	.045605
NA	.733000	.719662	.013338	.018196
PB	1.220000	1.219411	.000589	.000483
ZN	.330000	.331376	-.001376	-.004169

STANDARD ERROR OF ESTIMATE -- INDEX OF FIT

.2848378

Table V-5. Fit heavy industrial ambient aerosol with 6 emission sources

SOURCE COEFFICIENTS

COAL	AUTO	FOASH	CEMENT	IR&ST	CSOILD	SUM
.1041	.0303	.0802	.0549	.1287	.1284	.5266

UW-MEA: UNWEIGHTED MEASURED AEROSOL PROFILE
 UW-COM: UNWEIGHTED COMPUTED AEROSOL PROFILE
 UW-RES: UNWEIGHTED RESIDUAL
 W-RES: WEIGHTED RESIDUAL

ELEMENT	UW-MEA	UW-COM	UW-RES	W-RES
AL	1.820000	2.016889	-.196889	-.108181
CA	5.820000	5.725492	.094508	.016239
CU	.230000	.228854	.001146	.004984
MG	3.570000	3.286137	.283863	.079514
MN	.314000	.335995	-.021995	-.070048
NA	.733000	.728139	.004861	.006632
PB	1.220000	1.221688	-.001688	-.001384
ZN	.330000	.294706	.035294	.106950

STANDARD ERROR OF ESTIMATE -- INDEX OF FIT
 .1317290

Table V-6. Fit rural ambient aerosol with 7 emission sources

SOURCE COEFFICIENTS

COAL	AUTO	FOASH	CEMENT	IR&ST	ASOILD	CSOILD	SUM
.0538	.0128	.0574	.0487	.0165	.0246	.1262	.3399

UW-MEA: UNWEIGHTED MEASURED AEROSOL PROFILE
 UW-COM: UNWEIGHTED COMPUTED AEROSOL PROFILE
 UW-RES: UNWEIGHTED RESIDUAL
 W-RES: WEIGHTED RESIDUAL

ELEMENT	UW-MEA	UW-COM	UW-RES	W-RES
AL	1.690000	1.449144	.240856	.142518
CA	4.630000	4.688904	-.058904	-.012722
CU	.065400	.042437	.022963	.351112
MG	2.450000	2.447883	.002117	.000864
MN	.057400	.066348	-.008948	-.155895
NA	.426000	.460555	-.034555	-.081114
PB	.522000	.520907	.001093	.002095
ZN	.059000	.062991	-.003991	-.067641

STANDARD ERROR OF ESTIMATE -- INDEX OF FIT

.4233396

Table V-7. Fit rural ambient aerosol with 7 emission sources weight Cu by 1/10

SOURCE COEFFICIENTS

COAL	AUTO	FOASH	CEMENT	IR&ST	ASOILD	CSOILD	SUM
.0642	.0129	.0443	.0519	.0112	.0656	.1089	.3588

UW-MEA: UNWEIGHTED MEASURED AEROSOL PROFILE
 UW-COM: UNWEIGHTED COMPUTED AEROSOL PROFILE
 UW-RES: UNWEIGHTED RESIDUAL
 W-RES: WEIGHTED RESIDUAL

ELEMENT	UW-MEA	UW-COM	UW-RES	W-RES
AL	1.690000	1.686514	.003486	.002063
CA	4.630000	4.630852	-.000852	-.000184
CU	.065400	.032169	.033231	.050812
MG	2.450000	2.449969	.000031	.000013
MN	.057400	.057529	-.000129	-.002256
NA	.426000	.426500	-.000500	-.001174
PB	.522000	.521984	.000016	.000030
ZN	.059000	.059058	-.000058	-.000979

STANDARD ERROR OF ESTIMATE -- INDEX OF FIT

.0509271

The calculated lead source coefficient in Table V-7 was similarly confirmed.

Furthermore, it should be noted that high sodium levels in ambient aerosols exist due to road salt application. A road salt emission profile was not considered here. Therefore, a source reconciliation for a typical winter sample should exhibit measured sodium concentrations that exceed computed values. The overall fit should also be disturbed by the incomplete data. Table V-8 shows both these phenomena for a rural aerosol from late January.

More widespread use of the reconciliation model used here is envisioned. Recent controversies between alleged emitters and government regulatory agencies over the extent of industrial contributions accentuates the need for more sophisticated interpretation techniques than are now employed. The primary requirement at this stage is accurate ambient and emission profiles to incorporate into models which will generate undisputed source reconciliation.

Table V-8. Fit rural, winter ambient aerosol with 7 emission sources

SOURCE COEFFICIENTS

COAL	AUTO	FOASH	CEMENT	IR&ST	ASOILD	CSOILD	SUM
.0951	.0055	.2073	.0412	-.0047	.2454	-.0807	.5091

UW-MEA: UNWEIGHTED MEASURED AEROSOL PROFILE
 UW-COM: UNWEIGHTED COMPUTED AEROSOL PROFILE
 UW-RES: UNWEIGHTED RESIDUAL
 W-RES: WEIGHTED RESIDUAL

ELEMENT	UW-MEA	UW-COM	UW-RES	W-RES
AL	1.860000	2.150829	-.290829	-.156360
CA	1.660000	1.652452	.007548	.004547
CU	.035100	.041693	-.006593	-.187847
MG	.815000	.815234	-.000234	-.000287
MN	.039200	.035040	.004160	.106129
NA	2.430000	1.309200	1.120800	.461235
PB	.241000	.241232	-.000232	-.000964
ZN	.053400	.050141	.003259	.061028

STANDARD ERROR OF ESTIMATE -- INDEX OF FIT

.5361732

REFERENCES - V

1. Mayrsohn, H. and J. H. Crabtree. Source Reconciliation of Atmospheric Hydrocarbons. *Atmos. Env.*, 10:137-143, 1976.
2. Gatz, D. F. Relative Contributions of Different Sources of Urban Aerosols: Application of a New Estimation Method to Multiple Sites in Chicago. *Atmos. Env.*, 9:1-18, 1975.
3. Friedlander, S. K. Chemical Elemental Balances and Identification of Air Pollution Sources. *Environ. Sci. Technol.*, 7:235-240, 1973.
4. Greenberg, R. R., G. E. Gordon and W. H. Zoller. Composition of Particles Emitted from the Nicosia Municipal Incinerator. *Environ. Sci. Technol.*, 12:1329-1331, 1978.
5. Klein, D. H., A. W. Andren, J. A. Carter, J. F. Emery, C. Feldman, W. Fulkerson, W. S. Lyon, J. C. Ogle, Y. Talmi, R. I. Van Hook and N. Bolton. Pathways of Thirty-seven Trace Elements through Coal-fired Power Plant. *Environ. Sci. Technol.*, 9:973-979, 1975.
6. Andren, A. W. and S. E. Lindberg. Atmospheric Input and Origin of Selected Elements in Walker Branch Watershed, Oak Ridge, Tennessee. *Water, Air and Soil Pollution*, 8:199-215, 1977.
7. Miller, M. S., S. K. Friedlander and G. M. Hidy. A Chemical Element Balance for the Pasadena Aerosol. *J. Colloid and Interface Sci.*, 39:165-176, 1972.
8. Murphy, T. J. Sources of Phosphorus Inputs from the Atmosphere and their Significance to Oligotrophic Lakes. *Water Resources Center, University of Illinois, Urbana. Research Report No. 92*, 1974.
9. Draftz, R. G. Types and Sources of Suspended Particles in Chicago. Report No. IITRI-C9914-C01, Dept. of Environ. Control, Chicago, 1975.

APPENDIX V-A. SOIL ANALYSES

Table V-A-1. Metal analyses (%) of agricultural soil samples from the Menomonee River Watershed

Element	Subsample			Subsample		
	1	2	Mean	1	2	Mean
<u>Tilled Agricultural</u>			<u>Untilled Agricultural</u>			
Al	6.67	6.51	6.6	6.30	6.28	6.3
Ca	1.43	1.51	1.5	1.33	1.73	1.5
Cu	0.00318	0.00206	0.0026	0.00267	0.00292	0.0028
Fe	3.10	3.28	3.2	3.30	3.38	3.3
K	1.85	1.95	1.9	1.95	1.87	1.9
Mg	1.19	1.26	1.2	1.09	1.19	1.1
Mn	0.0898	0.0936	0.092	0.0962	0.106	0.10
Na	0.834	0.769	0.80	0.881	0.797	0.84
Pb	~0.001	~0.001	0.001	~0.001	~0.001	0.001
Zn	0.0117	0.0120	0.012	0.0110	0.0108	0.011
<u>Organic Agricultural</u>			<u>Mean Agricultural</u>			
Al	5.82	6.12	6.0	6.3		
Ca	1.65	1.70	1.7	1.6		
Cu	0.00498	0.00427	0.0046	0.0034		
Fe	3.11	2.99	3.1	3.2		
K	1.60	1.66	1.6	1.8		
Mg	0.891	0.901	0.90	1.1		
Mn	0.0530	0.0519	0.053	0.082		
Na	0.774	0.750	0.76	0.080		
Pb	~0.001	~0.001	0.001	0.001		
Zn	0.0148	0.0137	0.014	0.012		

Table V-A-2. Metal analyses (%) of construction site soil samples from the Menomonee River Watershed

Element	Subsample		Mean
	1	2	
Al	5.14	5.29	5.2
Ca	11.5	9.89	10.7
Cu	0.00266	0.00258	0.0026
Fe	2.83	2.85	2.8
K	2.00	2.07	2.0
Mg	6.53	6.19	6.4
Mn	0.0658	0.0624	0.064
Na	0.466	0.475	0.47
Pb	~0.001	~0.001	0.001
Zn	0.00725	0.00809	0.0077